FINAL REPORT

DEGRADATION OF COKE IN THE BLAST FURNACE

by

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The Final Report of the Project On

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1. INTRODUCTION AND LITERATURE REVIEW

In iron blast furnaces coke provides permeability, reductant and heat. Carbon monoxide and heat are generated in the raceways. Iron ore agglomerates are reduced by carbon monoxide to result in carbon dioxide and metallic iron. CO_2, the gaseous reaction product of iron ore reduction, may or may not react with carbon in coke, depending on temperature and CO/CO_2 ratio in the gas. Even when the solution loss reaction, i.e.,

$$C + CO_2 \rightarrow 2CO,$$

is thermodynamically favourable, the extent of the completion of this reaction before the gas leaves the furnace top depends on the kinetic nature of the system. The gas flow in the blast furnace is usually very turbulent; therefore, for a given temperature and gas composition, the property of coke often determines the kinetic behaviour of solution loss reaction. The reactivity of cokes is often defined by the reaction rates of solution loss reaction of cokes of given size under the same experimental conditions.

An overly reactive coke, in relation to a particular kind of iron ore agglomerate, may have several types of adverse effects in an iron blast furnace. This is mainly due to the fact that a larger fraction of carbon in the coke would be gasified in a strongly endothermic reaction before it could reach the raceways. The following are among the adverse effects of an overly reactive coke:

1. Weaker coke gives rise to problems related to impaired permeability in the lower part of the blast furnace.
2. More heat is consumed in the middle part of the blast furnace.
3. Less heat is available in the raceways from a given amount of coke charged to the blast furnace.
4. More CO is generated by solution loss reaction at lower temperature (i.e., nearer to the exit for the gas) to result in less efficient use of CO as a reductant.

All these effects will contribute to a less energy efficient, more irregular operation, lower productivity and shorter lining life of the blast furnace.

Due to its obvious importance, the reactivity of metallurgical coke has been the subject of many studies, which has led to a variety of explanations. The difficulty in the characterization of such highly heterogeneous solids such as coke is likely to be the main source of the problems. The opinions on the possible significance of the variation of coke reactivity on the performance of a blast furnace because of the added variables in iron ore and in operational conditions, are even more diversified.

Schapiro and Gray[1] reviewed relevant literature and investigated reactivity of cokes which were made from coals and blends of U.S. Steel Corp. The weight loss (daf) of coke specimens (minus 4 plus 6 mesh) in pure CO_2 at 2000°F (1093°C) for 30 minutes was reported as reactivity. They found reactivity is proportional to initial pore volume. Based on cokes from single coals, the reactivity as a function of rank of coal has a minimum value when

the coal is in the middle of the range of the rank. These conclusions were supported by the findings of Benedict and Thompson[2]. They showed that coke reactivity relates to both the reflectance (or rank) and the effective (exposed) inert content of the initial coals. It was reported that the thickness of the pore wall, pore volume and size are important with implications on surface area accessible to the reacting gas. Cokes from low rank coals are more reactive because of more open structure and more reactive carbon form, amorphous types. Reactivity was found to increase linearly with porosity and to decrease linearly with the increase of wall thickness.

Twenty-one U.S. coals, of wide range of rank from lignite to anthracite, were carbonized in the laboratory and the reactivites in air at 500°C of the resulting char or coke were measured by Jenkins, Nandi and Walker[3]. Some of these coals were demineralized in acids before carbonization. They found that reactivity of these single-coal cokes depends on the rank of coal, amount and composition of ash, pore structure and carbonization temperature. The reactivity decreases with the increase of carbon content (wt.%, daf). Among coals investigated, cokes with high magnesium and calcium levels are highly reactive. Cokes with a higher level of macro and transitional porosity (the "feeder" pores) are highly reactive since the ability of a reactant gas to diffuse into the internal surface of the micropore is enhanced. Reactivity of cokes decreases with the increase of carbonization temperature. This result could be explained in terms of diminishing hydrogen content, surface area, and "feeder" pores as the result of higher carbonization temperature.

The selective or preferential oxidation of structural components was discussed by Taylor and Marsh[4] and of carbon forms was suggested by several Japanese authors[5] based on specimens obtained in the dissection of commercial blast furnaces. Lu, Samaan and Uribe[5] also reported that isotropic carbon is the most reactive and coarse mosaic is the least reactive, based on single-coal cokes.

A comprehensive study on this subject has been carried out by Chiu[6]. Twenty coals and four blends were carbonized in 15 lb. and 500 lb. test ovens under standardized conditions. For reactivity measurement, cokes of 20 ± 1 mm size were used. Specimens were reacted with pure CO_2 at 1050°C for two hours followed by drum test for measuring the strength after reaction. The selectivity of oxidation of carbon forms was confirmed by Chiu. He reported that mosaic and flow-type structures have higher resistance to CO_2 oxidation. No relationship between reactivity and porosity could be detected in his data. With respect to the rank of coals studied, the reflectance of vitrinite in oil ranges from 0.7 to 1.6. The reactivity decreases very slightly with the increase of reflectance for North American and Taiwanese coal but significantly for Australian coals. The influence of ash was expressed in metal oxide content in coke which is defined as the sum of Fe_2O_3, CaO, MgO, Na_2O and K_2O. He found an increase of reactivity with the increase of metal oxide content but also pointed out that the quantitative relationship depends on the country of origin.

Among the references cited, the above two papers[5,6] were concerned with the loss of strength as the result of carbon gasification. Chiu[6] stated that there is a relationship between properties of cokes made of individual coals, and those made of blends. Petrographic composition, chemical composition and reactivity of cokes made from blends are the weighted average

of values of single-coal cokes. This is not so for physical properties such as coke strength M_{30} and after-reaction-strength (+ 10 mm).

2. OBJECTIVES OF THE PRESENT WORK

After our preliminary success in the study of selectivity of oxidation of different carbon forms[5] in single-coal cokes, it was proposed to extend this work to commercial cokes. It was intended to establish certain relationships experimentally between carbon texture in commercial cokes and their chemical properties with respect to carbon dioxide and potassium vapour. The existence of such relationships relevant to cokes of importance to Canadian steel companies would contribute to the future imporvement of blending and coking operations in Canada.

3. COKE SAMPLES FROM STEEL COMPANIES

We contacted three Canadian steel companies to inform them of this project and requested that they provide samples of interest to them. One set of samples is labelled as Al-1, Al-2 and Al-3. They were sent to us without information, other than that they have different reactivities, so that investigators in this project would not have any pre-conceived ideas or anticipation of the data. Recently we received relevant data of these commercial cokes made from the same blend. They are listed in Table 1.

Table 1 Manufacturer's data of cokes Al-1, Al-2 and Al-3

Coke Sample	Al-1	Al-2	Al-3
Coking time, hr.	26.7	18.5	24.1
Reactivity, %	14.54	6.02	27.64
Stability	64.2	61.5	61.7
Hardness	69.7	68.0	68.3
Low volatile coal in the blend, %	35.0	35.0	35.0
Ash, %	8.18	7.6	8.7
Sulphur	0.59	0.69	-
Volatile matter in coke	1.31	0.9	3.20
These cokes were made from essentially the same blend. The main difference is in final temperature reached, as indicated in volatile matter contents. The final temperature for Al-3 might be 30°C lower.			

The second set of samples S-A, S-B and S-C were supplied by another Canadian company. The information recently made available is given in Table 2.

Table 2 Manufacturer's data of cokes S-A, S-B and S-C.

Coke Sample	S-A	S-B	S-C
Coke plant	H	H	L
Blend:			
LV(R_o = 1.6)	22	22	22
L-MV(R_o = 1.4)	6	6	6
H-MV(R_o = 1.0)	50	50	57
HV"a"(R_o = 0.80)	20-25	20-25	15
S-A and S-C are normal commercial cokes of good stability. S-B was made during abnormal but stable conditions with residence time of coke in the oven nearly two days.			

Another set of eight cokes has been provided by this company with detailed information for the next stage of the work.

The coke sample labelled Re-1 is of U.S. origin. It is a single-coal coke made in a movable wall oven. The following information was provided by its manufacturer.

Stability 52

	Coal	Coke
Ash, %	5.6	7.5
Sulfur, %	0.8	0.7
Volatile Matter, %	29.4	

In our laboratory, there are coke samples of European origins for other projects. A few measurements will be done on these cokes.

4. APPARATUS FOR POTASSIUM VAPOUR GENERATION AND ABSORPTION

The assembly consists of two vertical electrical resistance heated furnaces, with the larger furnace located right above the other. The details were documented in last year's report. The argon-potassium vapour mixtures are prepared by bubbling de-oxidized argon through liquid potassium in the lower furnace. The mixture is then introduced directly to the bottom of the

upper or larger furnace where carbonaceous materials are placed for potassium absorption. Special care was taken in the design and construction of this two-furnace assembly that there would be no condensation of potassium vapour or any side reaction that could take place in between the two furnace chambers.

In blank experiments (i.e., there were no carbonaceous materials in the larger furnace to absorb potassium vapour from the gaseous mixture), losses of potassium in the upper furnace were noticed based on chemical analysis and mass balance calculation. The cause was determined to be condensation of potassium on the top plate of the upper furnace. This problem was solved by applying insulating material on the top plate of the upper furnace as shown in Fig. 1. Such improvement was found to be adequate by determining the temperature profile (i.e., the minimum temperature in the upper furnace is higher than the maximum temperature used in the lower furnace in the present work), as shown in Fig. 2 and by mass balance as shown in Fig. 3.

5. CALIBRATION OF PARTIAL PRESSURES OF POTASSIUM AND THE DETERMINATION OF OPTIMUM CONDITIONS FOR VARPOURIZATION

The results of this section are shown in Figs. 4 to 10. The argon bubbling arrangement is shown in Fig. 4. A minimum residence time of each bubble in the melt is required to ensure the saturation of potassium vapour. The distance (which is related to residence time) for the bubble to travel or the depth of melt above the nozzle is defined as H_1; see Fig. 4. Three experiments with different values of H_1 under otherwise identical conditions were carried out and results given in Fig. 4. It proves that the depth of 45 mm is definitely inadequate; however, one does not know whether or not 80 mm is enough.

The results concerning the influence of argon flow rate and temperature of the potassium melt are given in Figs. 5 and 6 for shallow melt and Figs. 7 and 8 for deep melt. The measured partial pressure of potassium is obtained by collecting and analyzing potassium trapped in absorbing bottles from the exhaust gas from the upper furnace and measured argon flow rate. The calculated partial pressure is done from thermodynamic data. Assuming the flow rate of argon is accurately measured, the ratio of measured to calculated partial pressure of potassium should be 1.0 or less. The value of unity corresponds to the ideal case. This means that the vapourization reaches the equilibrium state in the lower furnace; there is no condensation or side reactions involving the gaseous phase in the whole assembly; and the removal of potassium from the exhaust gas is complete. The decrease of the ratio of P_{KM} to P_{KC} with increase of argon flow rate as well as melt temperature (Figs. 5 and 6), may be explained by channelling rather than bubbling of argon through the shallow melt. The increase of melt temperature will result in an increase of actual volumetric flow rate of gas even though there is no change in mass flow rate. On the other hand, when the depth and temperature of the melt and argon flow rate were high, the ratio was over the theoretical limit, unity; see Figs. 7 and 8. This may be explained by the splashing of the liquid metal to produce suspended fine droplets of liquid potassium in the argon stream.

The generally accepted values of partial pressure of potassium in the blast furnace under ordinary conditions are in the range 10^{-4} to 10^{-2} atm. When the melt is at 410°C its vapour pressure is reported to be 3×10^{-3} atm. As an example, the results at 410°C are shown in Figs. 9 and 10 to demonstrate the effect of argon flow rate and the depth of the melt. The optimum argon flow at 410°C is chosen to be slightly above 4.0 ml/sec because the ratio of P_{KM} to P_{KC} is closer to 1.0 and relatively insensitive to the depth of the melt. For experiments to be conducted at other melt temperatures the same procedure would apply. Some numerical results are listed in Table 3 for future reference.

6. CHEMICAL ANALYSIS OF POTASSIUM IN COKE

At high temperatures under reducing or neutral atmosphere, potassium in coke may be either associated with carbon to form intercalation compounds or as part of mineral matter. The physical and chemical effects of potassium in coke (i.e., fissure formation and catalytic effect of solution loss reaction) should be contributed by the portion which is with carbon. It is desirable to differentiate these two types of potassium in coke in chemical analysis. Monson[7] has reported that it was very fruitful to do so in the effort to explain the degradation of coke in commercial blast furnaces. The extent of degradation of coke in the blast furnace was found to be proportional to the increase of "water soluble" potassium in tuyere coke in comparison with samples taken in the stockhouse. The two types of procedures used are shown schematically in Fig. 11.

Fig. 12 shows the nature of the problems we still have to overcome. The oxidation rate by atomic oxygen at 100 to 120°C was slow and the residue carbon was high even after long exposure time. At low temperature it might be limited by having atomic oxygen contact the interior carbon without being deactivated first. At high temperature, it might be the formation of a coating of low melting glass, particularly after potassium absorption. Intermittent crushing during both steps of ashing has moderated the problems stated above.

Two sizes of coke samples for ashing were compared and the results are given in Figs. 13 to 16. The smaller sample (0.05 gm) resulted in higher water soluble potassium and sodium contents, most likely due to the higher degree of gasification of carbon. This is because more alkali intercalation compounds would convert to oxides and carbonates. During high temperature ashing in a muffler furnace, it is conceivable that some weaker compounds of alkalies may be gasified after reduction by carbon in the interior of the powder packing or the center of a large enough particle, where oxygen potential may not be high. These weaker compounds may originate from intercalation compounds or an ash particle excessively enriched with alkalies. Both factors contribute to the higher reading in smaller samples, as summarized in Fig. 16.

The analytical results of acid soluble alkalies for both large and small samples, with or without low temperature plasma pre-treatment, are compared in Figs. 17 and 18. The scattering is still too large to be acceptable; however, systematic error is only for sodium.

Table 3 Data of the calibration of potassium partial pressure in Ar-K mixtures.

Experiment No.	P_{KM} (Measured)	P_{KC} (Calculated)	$\lambda = P_{KM}/P_{KC}$	F_{Ar} (ml/sec)	P_{Ar} (kg/cm^2)	Potassium Temp. (°C)	Time (sec)	Potassium Depth H_1 (mm)	Ref.
1	4.51×10^{-5}	4.24×10^{-5}	1.06	2.5	1.406	242	900	34.65	
2	4.35×10^{-5}	4.24×10^{-5}	1.02	4.0	1.406	242	900	34.65	
3	4.38×10^{-5}	4.34×10^{-5}	1.00	4.0	1.406	242	2700	34.65	
4	4.23×10^{-5}	4.34×10^{-5}	0.97	7.0	1.406	242	900	34.65	
5	2.33×10^{-3}	3.09×10^{-3}	0.75	4.0	1.406	412	900	34.65	
6	2.06×10^{-3}	2.73×10^{-3}	0.76	7.0	1.406	407	900	34.65	
7	2.43×10^{-3}	2.46×10^{-3}	0.98	4.0	1.406	403	2700	34.65	
8	2.66×10^{-3}	3.42×10^{-3}	0.78	4.0	1.406	416	900	60.00	
9	5.47×10^{-3}	3.42×10^{-3}	1.60	7.0	1.406	416	900	60.00	
10	8.41×10^{-5}	2.42×10^{-4}	0.35	2.5	1.406	311	900	80.00	
11	1.28×10^{-4}	2.42×10^{-4}	0.53	7.0	1.406	311	900	80.00	
12	3.35×10^{-4}	2.86×10^{-3}	0.12	2.5	1.406	409	900	80.00	
13	4.52×10^{-3}	2.86×10^{-3}	1.57	7.0	1.406	409	900	80.00	
14	2.04×10^{-3}	3.51×10^{-3}	0.58	4.0	1.406	417	900	80.00	

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For the total amount of potassium in coke, shown in Fig. 19 as an example, it appears necessary to include the step of low temperature ashing and leaching before high temperature ashing. As demonstrated in Fig. 20 X-ray fluorescence does not seem promising either.

At the present time we are working with our colleagues in the Department of Engineering Physics to develop a better procedure of low temperature ashing with much more powerful energy source available in that department.

7. KINETICS OF COKE OXIDATION BY Ar-CO_2-CO MIXTURES

The experimental conditions were selected to ensure that oxidation will take place under the condition that the rate-controlling step is essentially interfacial chemical reaction. The reaction temperatures are low and the layers of coke powders are thin.

The thermodynamic driving force was lowered by including CO in the incoming gas so that carbon crystals in different energy states hopefully may be reflected in the variation of reaction rate among carbon of different optical textures.

As examples, the results of oxidation experiments of four types of cokes are plotted in Figs. 21 and 22 with weight loss vs. reaction time. In all experiments for all cokes the same gas composition ($Ar/CO_2/CO$ = 50/45/5 by volume) and the same total flow rate (4.0 ml per second measured at room temperature was used. The reaction temperature for cokes as received was 950°C and 850°C with prior potassium impregnation. The reaction rates are expressed in percentage of weight loss per unit time and appear to be constant in time under conditions studied for all cokes.

As established in our work in 1981, in th preparation of specimens for the study of changes of optical texture due to partial gasification, it is desirable to have about 20% burn-off. It would allow the changes in most types of carbon to be observable, and would be a degree of burn-off similar to that of cokes in commercial blast furnaces. The specific conditions for the preparation of these specimens are given in Table 4. The reaction rates are listed in Table and also plotted in Fig. 23.

8. THE ANALYSIS OF OPTICAL TEXTURE OF CARBON FORMS IN COKE

As we stated in our early reports, we follow the classification and procedures used by BCRA in our texture analysis. In order to facilitate the communication between our group and the Scientific Authority of this project, a photo album showing typical textures of Canadian coke which we use for the training in inexperienced research workers was sent to CANMET last year. Mr. T.T. Le who started as a research assistant for this project and is now a graduate student, was trained by Mr. Marco Uribe. Mr. Vladimir Kupec replaced Mr. Le officially on September 1, 1982. In all cases, the minimum number of counts of each specimen was 300. Many specimens were analyzed independently by both Mr. Le and Mr. Kupec. In the cases compared, the

Table 4 Reaction Rates of Carbon Gasification With and Without Potassium Impregnation

Coke Specimen	Potassium Impregnation (%)	Oxidation Temperature (°C)	Reaction Time (hrs.)	Weight Loss ΔW (%)	ΔW/t (%/hr.)
Al-1	-	950	6.00	20.00	3.23
	3.3	850	1.00	17.20	17.20
Al-2	-	950	9.00	19.40	2.15
	5.1	850	1.50	23.40	15.60
Al-3	-	950	2.00	18.00	9.00
	4.0	850	0.75	26.40	35.20
Re-1	-	950	6.00	25.00	4.16
	5.4	850	1.00	24.40	24.40
S-1	-	950	6.00	23.00	3.80
	3.8	850	1.50	19.80	13.20
S-2	-	950	6.00	25.70	4.30
	4.5	850	1.0	20.30	20.30
S-3	-	950	6.00	19.80	3.30
	4.3	850	1.50	18.90	12.60

Gas Composition: $Ar/CO_2/CO = 50/45/5$

Gas Flow Rate: 4 ml/sec. measured at room temperature

Diameter of Reaction Tube: 58 mm

agreement between the two experimentalists is very reasonable. The convergence or stability of the readings, using Coke Al-1 as an example, is shown in Fig. 24. The experimentalists were advised to take fifty counts only each time, so that their eyes would not be over-strained. For this reason data were recorded in lots of fifty counts. In Fig. 24 the actual number of counts in each lot was shown on the vertical axis and the accumulative total number of counts is shown on the horizontal axis. In addition to Coke Al-1 as received, Al-1 after oxidation, after impregnation and impregnation/oxidation were also included in Fig. 24 for comparison.

(a) The Impregnation of Potassium

Coke specimens in powder form (in the size range from 500 to 600 μm) were exposed to Ar-K atmosphere at 1000°C for 45 minutes, except Coke S-B. In each run, three screen dishes each containing one gram of coke powders were positioned at the same level and equal distance from the gas inlet below. Specimens were placed in the upper and larger furnace at room temperature and heated in a gentle flow of pure argon (0.25 ml/sec at room temperature) by-passing the smaller furnace. Usually the temperature reached the desired value of 1000°C in about two hours. At that time the heating of the small furnace containing metallic potassium, started. After about one hour and 35 minutes the small furnace reached the pre-determined temperature of 420°C; then the gentle flow of argon of 0.25 ml/sec to the small furnace and an increased flow of argon directly to the large furnace (by-passing the small furnace) started. It took about 20 minutes to stabilize the flows and temperatures before directing the main flow through the small furnace, i.e., the pool of liquid potassium metal, and turning off the direct flow to the large furnace. The experiments were terminated after 45 minutes from this moment.

The conditions adopted here for potassium impregnation are to ensure that the partial pressure of potassium would be as close as possible to the equilibrium value yet the total flux of potassium large enough to sustain the chemical reaction.

Different specimens did absorb different amounts of potassium under supposedly idential conditions as listed in column two of Table 5. At the present time, we don't want to emphasize such differences because the values of potassium absorbed by powders in three dishes in a single experiment do not duplicate each other to our satisfaction yet.

In Table 5, the results of optical texture analysis of each coke specimen as received and that after potassium impregnation are listed. In most cases, the differences in values due to potassium impregnation are much larger than possible errors in counting. Simple calculations based on data listed in Table 5 were carried out (as shown in Table 6) and the results are given in Table 7. As an example, the changes in the composition of carbon textures are listed in the third row of Table 6. In this particular case, the total increase is 11.33 and of course, the total decrease is of the same value. The distributions of the increase and the decrease among different types of carbon are obtained by having the values in row three divided by 11.33 (100%), as listed in row four and row five, respectively. Row six is the corresponding values for the sub-total for each group.

Table 5 Optical Texture Analysis of Coke Specimens Before and After Potassium Absorption

Coke Specimen	K Impregnation	--Isotropic & Inert--			----------Mosiac----------					------Other Flow Types------			
		Isot.	Inert	Sub Total	Fine	Medium	Coarse	Sub Total	Granular Flow	Creased	Ribbon	Flat	Sub Total
A1-1		0	6.33	6.33	10.66	14.67	33.67	59.00	9.33	15.67	5.67	4.00	25.34
	3.3% K	0	7.00	7.00	7.33	12.00	42.00	61.33	6.00	13.67	6.67	5.33	25.67
A1-2		0.66	10.00	10.66	10.00	13.00	26.67	49.67	15.67	18.00	3.60	2.30	24.00
	5.1% K	0	10.50	10.50	3.00	9.00	35.60	47.60	24.60	11.60	3.30	2.30	17.30
A1-3		0.33	13.67	14.00	15.65	23.64	21.31	60.60	7.42	10.32	4.33	3.33	17.98
	4.0% K	0.33	10.33	10.66	13.33	33.67	21.67	68.67	7.67	7.67	2.00	3.33	13.00
Re-1		0.33	9.00	9.33	3.33	1.33	46.00	50.66	33.67	6.00	0.33	0	6.33
	5.4% K	0.33	10.67	11.00	0.33	0	6.33	6.66	79.33	2.67	0.33	0	3.00
S-A		8.66	21.66	30.32	19.67	23.00	7.67	50.34	8.33	6.00	3.00	2.00	11.00
	2.72% K	0	16.00	16.00	1.33	7.33	54.00	62.66	13.33	4.67	2.67	0.66	8.00
S-B		7.66	20.66	28.32	12.33	28.00	10.66	50.99	9.30	7.33	3.33	0.66	11.32
	8.83% K	3.67	15.00	18.67	5.67	16.67	33.33	55.67	17.33	4.33	2.00	2.00	8.33
S-C		1.40	18.80	20.20	1.30	12.30	31.50	45.10	21.20	5.30	4.0	4.20	13.50
	3.11% K	0	16.00	16.00	0.30	4.50	38.30	43.10	31.30	2.00	4.60	3.00	9.60
S-HV				15.30	22.50	57.50	3.00	83.00	1.20	0.50	-	-	0.50
S-LV				22.50	0.10	1.40	10.50	12.00	21.50	41.10	-	2.90	44.00

Optical texture analysis is based on at least 300 counts, which were carried out following BCRA procedures.

*S-HV and S-LV are cokes made in the laboratory and the rest are commercial cokes made in Canada.

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Table 6 Changes in Optical Texture of Commercial Coke A1-1 Due to the Absorption of Potassium Vapour

	--Isotropic & Inert--			----------Mosiac----------					------Other Flow Types------			
	Isot.	Inert	Sub Total	Fine	Medium	Coarse	Sub Total	Granular Flow	Creased	Ribbon	Flat	Sub Total
Coke as received Optical texture, %	0	6.33	6.33	10.66	14.67	33.67	59.00	9.33	15.67	5.67	4.0	25.34
After K absorption, 3.3% wt. Optical texture, %	0	7.0	7.0	7.33	12.0	42.0	61.33	6.0	13.67	6.67	5.33	25.67
Final state - initial state		0.67	0.67	-3.33	-2.67	8.33	2.33	-3.33	-2.00	1.0	1.33	0.33
Percentage of the increase		5.9				73.0				8.8	12.0	
Percentage of the decrease				-29.0	-23.0			-29.0	-17.0			
			5.9				21.0	-29.0				2.9
After K absorption and gasification by CO_2 with 17.2% burn-off Optical texture, %	5.34	11.33	16.67	3,33	23.0	30.0	54.33	8.67	12.0	4.33	4.0	20.33
RMR, % *		-2.69	-6.64	4.34	-1.59	1.6	1.46	1.41	2.19	2.20	1.09	2.02

*RMR calculated based on the optical texture after potassium absorption.

In Table 7, the values corresponding to row three and combined rows four and five in Table 6 for all cokes studied so far are listed. For each coke the first row shows the magnitude of the changes due to potassium impregnation, including the sign (positive for an increase and negative for a decrease). The values in the second row show the relative contributions among various types of carbon to the total increase as well as to the decrease.

The effect of the potassium absorbed on the changes in the optical texture of coke specimens can be easily visualized in Table 7. A decrease in isotropic, fine mosaic and creased flow carbons were observed in all specimens examined. The trend in showing a decrease is very strong in inert and medium mosaic structures. The observed increases are mainly for the larger grains, i.e., coarse mosiac and granular flow. The exception is Coke Re-1, a single-coal coke from the United States, that shows a clear conversion from coarse mosaic to granular flow. The Coke Al-1 shows a different pattern of changes; however, the magnitude of these conversions is not large.

(b) The Relative Micro Reactivity (RMR)

RMR is a measure of relative reactivity of the co-existing different types of carbon with respect to oxidation by Ar-CO_2-CO mixture. It is the percentage of each type of carbon which disappeared during the course of oxidation reaction which is normalized by the overall degree of burn-off of the specimen. The detailed computation to obtain RMR is given in Table 8 using Coke Al-1 as an example. The RMR values of carbons of particular textures and their corresponding physical significance, are given below:

RMR > 1.0	More reactive than the average of the whole specimen
RMR = 1.0	Same as the average
1.0 > RMR > 0.0	Less reactive than the average
RMR = 0	No change
RMR < 0.0	A net increase of this type of carbon
RMR = $-\infty$	A net increase, the initial value was zero

In Table 9, the values of RMR for cokes which have been analyzed for their optical texture (see Table 4) up to the present time, are listed. Comparing the average value of each column (which means that the individual characteristics of each coke are ignored for the moment), there is a pattern to be recognized. It is very clear that fine mosiac carbon is the most reactive one with respect to carbon dioxide oxidation. The average value of RMR for fine mosaic carbon is 3.57 and 2.05 for creased flow. Inert, medium mosaic and flat flow all have a RMR value very close to unity, i.e., reacted in a proportion the same as the degree of burn-off of the specimen. Coarse mosaic as reported in the literature is significantly less reactive compared with the whole specimen.

One may suggest that the increase of isotropic carbon which is contrary to the reports in the literature, is the result of incomplete reaction of

Table 7 Changes in Optical Texture Induced by Potassium Absorption

		--Isotropic & Inert--			--------Mosiac--------				---Other Flow Types----		
		Isot.	Inert	Sub Total	Fine	Medium	Coarse	Granular Flow	Creased	Ribbon	Flat
Al-1	Changes	-	0.67	0.67	-3.33	-2.67	8.33	-3.33	-2.00	1.0	1.33
	(%)	-	5.90	5.90	-29.00	-23.00	73.00	-29.00	-17.00	8.80	12.00
Al-2	Changes	-0.66	0.50	-0.16	-7.00	-4.00	8.93	8.93	-6.40	-0.30	-
	(%)	-3.60	2.72	-0.88	-38.12	-21.78	48.63	48.63	-34.85	-1.63	-
Al-3	Changes	-	-3.34	-3.44	-2.32	10.03	0.36	0.25	-2.65	-2.33	-
	(%)	-	-31.39	-32.33	-21.80	94.26	3.38	2.35	-24.90	-21.90	-
Re-1	Changes	-	1.67	1.67	-3.00	-1.33	-39.67	45.66	-3.33	-	-
	(%)	-	3.52	3.52	-6.34	-2.81	-83.82	96.47	-7.03	-	-
S-A	Changes	-8.66	-5.66	14.32	-18.34	-15.67	46.33	5.00	-1.33	-0.33	-1.34
	(%)	-16.87	-11.02	-27.89	-35.72	-30.52	90.25	9.74	-2.59	-0.64	-2.61
S-B	Changes	-3.99	-5.66	-9.65	-6.66	-11.34	22.66	8.02	-3.01	-1.34	1.32
	(%)	-12.47	-17.68	-30.15	-20.81	-35.37	70.81	25.06	-9.40	-4.18	4.12
S-C	Changes	-1.40	-2.80	-4.20	-1.00	-7.80	6.80	10.10	-3.30	0.60	-1.20
	(%)	-8.00	-16.00	-24.00	-5.71	-44.57	38.85	57.11	-18.85	3.42	-6.85

This table was prepared from data given in Table 5.

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Table 8 Relative Micro Reactivity (RMR) Based on Optical Texture Analysis of Commercial Coke A1-1

	--Isotropic & Inert--			----------Mosiac----------					------Other Flow Types------			
	Isot.	Inert	Sub Total	Fine	Medium	Coarse	Sub Total	Granular Flow	Creased	Ribbon	Flat	Sub Total
Coke as received (basis of calculation 100 gm coke)												
Optical texture, %	0	6.33	6.33	10.66	14.67	33.67	59.00	9.33	15.67	5.67	4.0	25.34
W, wt. of carbon (gm)*	0	5.82	5.82	9.81	13.50	30.97	54.28	8.58	14.41	5.22	3.68	23.31
After gasification by CO_2 with 20.0% burn-off												
Optical texture, %	3.3	10.10	13.4	5.6	14.0	42.6	62.3	8.3	9.00	4.40	2.6	16.0
Weight of carbon (gm)	2.37	7.27	9.65	4.03	10.08	30.67	44.86	5.98	6.48	3.17	1.87	11.52
ΔW, Weight loss (gm)	-2.37	-1.45	-3.82	5.78	3.42	0.30	9.42	2.6	7.93	2.05	1.81	11.79
(ΔW/W) 100%	- ∞	-24.91	-65.63	58.92	25.33	0.96	17.35	30.30	55.03	39.27	49.18	50.57
RMR	- ∞	-1.24	-3.28	2.95	1.26	0.048	0.86	1.51	2.75	1.96	2.45	2.53

where

$$RMR = \frac{(\Delta W/W)\ 100\%}{\text{Burn-off in \%}}$$

* The ash content of coke is assumed to be 8% for this calculation.

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Table 9 Relative Micro Reactivity (RMR) of Coke Specimens Before and After Potassium Absorption

		--Isotropic & Inert--			----------Mosiac----------					------Other Flow Types------			
		Isot.	Inert	Sub Total	Fine	Medium	Coarse	Sub Total	Granular Flow	Creased	Ribbon	Flat	Sub Total
Al-1		- ∞	-1.24	-3.28	2.95	1.26	0.048	0.86	1.51	2.75	1.96	2.45	2.53
	3.3% K	- ∞	-2.69	-6.64	4.34	-1.59	1.60	1.46	1.41	2.19	2.20	1.09	2.02
Al-2		-4.65	0.95	0.58	3.66	1.61	-0.99	0.62	1.78	2.82	-1.99	-0.12	1.81
	5.1% K	4.27	1.83	1.98	3.42	1.08	-0.26	0.83	0.61	2.38	-0.74	-1.71	1.52
Al-3		-26.30	2.28	1.62	1.84	-1.18	1.99	0.71	1.54	1.95	1.08	1.97	1.75
	4.0% K	-15.53	2.47	2.05	1.72	-0.47	1.67	0.84	0.63	0.82	2.75	1.08	1.33
Re-1		-10.93	1.62	1.18	3.71	1.80	3.53	3.50	-2.80	2.54	1.07	- ∞	2.32
	5.4% K	-14.34	1.53	0.98	4.09	4.09	3.27	3.34	-1.98	0.42	-11.18	- ∞	-0.49
S-A		-13.65	1.07	0.22	3.37	1.16	1.01	1.41	-11.11	2.63	2.23	2.07	2.75
S-B		- ∞	-0.11	-0.87	2.61	1.43	1.53	1.65	-4.11	0.92	-4.20	-2.98	-0.40
S-C		0.76	3.03	2.89	4.77	2.46	-0.67	0.71	-1.43	2.09	-3.62	4.31	2.14
S-HV				3.7	3.7	-0.43	-2.33	0.6	-2.12	4.7	-	-	4.7
	0.41% K			3.6	4.8	-0.87	-1.87	0.6	-1.90	4.2	-	-	4.2
S-LV				2.7	4.3	1.70	0.30	0.50	1.50	0.1	-	1.6	0.2
	0.67% K			2.6	4.4	2.0	0.60	0.80	1.10	0.2	-	3.4	0.4

Degree of burn-off for all specimens were in the range from 17.2 to 26.4%.

S-HV and S-LV are single-coal cokes made in the laboratory.

Table 10 Fractional Carbon Loss in Oxidation by Carbon Dioxide

		--Isotropic & Inert--			----------Mosiac----------					------Other Flow Types------			
		Isot.	Inert	Sub Total	Fine	Medium	Coarse	Sub Total	Granular Flow	Creased	Ribbon	Flat	Sub Total
Al-1		-11.87	-7.22	-19.09	28.94	17.01	1.48	46.48	12.95	39.62	10.23	9.01	58.97
	3.3% K	-22.99	-15.65	-38.64	42.57	-21.46	49.55	79.25	12.10	31.55	11.48	4.01	47.13
Al-2		-2.83	8.74	5.69	33.67	19.25	-24.29	28.33	25.67	46.99	-6.58	-0.25	39.82
	5.1% K	2.60	16.83	19.42	31.46	12.91	-6.38	37.93	8.79	39.41	-2.44	-3.62	33.44
Al-3		-7.89	28.65	20.86	26.49	-25.66	39.00	39.58	10.50	18.50	4.29	6.02	28.94
	4.0% K	-4.65	31.04	26.40	24.76	-10.22	32.73	46.83	4.30	7.78	10.94	3.30	22.00
Re-1		-3.27	13.41	10.12	11.35	2.19	149.38	163.14	-86.72	14.02	0.32	-0.84	13.50
	5.4% K	-4.30	12.66	8.40	12.51	4.98	138.38	155.68	-61.32	2.31	-3.35	-1.81	-2.85
S-A		-6.83	8.13	1.80	34.03	16.70	40.50	91.23	-36.66	28.93	5.35	4.35	42.90
S-B		-4.41	-0.64	-5.05	24.79	31.03	64.11	120.78	-12.33	6.16	-6.30	-4.47	-3.92
S-C		0.46	39.99	39.02	19.08	34.69	-20.50	34.-9	-15.30	19.86	-8.69	27.58	39.38
S-HV				52.54	77.33	-22.92	-6.52	46.20	-2.33	2.35	-	-	-2.35
	0.41% K			51.12	100.32	-46.37	-5.24	46.20	-2.09	2.10	-	-	-2.10
S-LV				56.43	0.43	2.21	2.94	5.60	30.00	3.82	-	4.32	8.10
	0.67% K			54.34	0.44	2.60	5.88	8.96	22.00	7.64	-	9.18	16.36

This table was prepared by multiplying the RMR by the weight of each type of carbon.

S-HV and S-L are single-coal cokes made in the laboratory.

fine mosaic. However, the unusual behavior of granular flow carbon has to be explained by other mechanisms. One of the possibilities is that the increase in granular flow carbon is the result of thermal treatment. When the rate of its formation exceeds the rate of gasification, then a net gain will result. If this were true, the increase in granular flow texture as listed in Table 7 could also be interpreted in the same manner.

The absorbed potassium in cokes did not show any pronounced or systematic changes in RMR, with two notable exceptions. Apparently, potassium in Coke A1-1 made the very inert mosaic carbon very reactive; at the same time the medium mosiac was exactly the opposite. It could also be considered that the partially reacted coarse mosaic assumed the appearance of medium mosiac structure. The second exception is the isotropic carbon in Coke A1-2; however, it may not be significant quantitatively, as shown in Table 10.

RMR is an intensive quantity that does indicate the actual contribution of each type of carbon to the observed weight loss. The actual value of ΔW, the weight loss of each type of carbon as defined in Table 8, divided by the degree of burn-off of the specimen and multiplied by 100%, is given in Table 10. Each of these positive numbers in this table shows the weight loss in arbitrary units of each type of carbon when the specimen as a whole experienced a weight loss of 100 units. For example, when Coke Re-1, as received, suffered a weight loss by CO_2 gasification of 100 mg, the amount of loss in coarse mosaic was 149.4 mg and the amount of gain for granular flow was 86.7 mg. The very drastic change of RMR of isotropic carbon in Coke A1-2 (see Table 9), may not be significant in view of the very minor role it plays quantitatively, as shown in Table 10. Based on the amount of each type of carbon involved, it is certainly possible that the newly created isotropic carbon was originated from fine mosaic structure. On the other hand, it is difficult to explain that the increase of coarse mosaic in Coke A1-2 during oxidation was solely due to the conversion from carbon which was initially of granular flow texture.

9. SURFACE AREA MEASUREMENT AND REACTIVITY OF COKES

Walker[8] has quoted a statement made by G.A. Simons and M.I. Finson that the pore system in chars (and cokes) resembles an ordinary river or tree system with small pores feeding into increasingly larger pores until eventually all pores lead into the main trunks. Walker et al.[13] suggested that surface measurement by nitrogen adsorption at liquid nitrogen temperature (the BET approach) only includes macro and transitional pores (the trunks and major branches of the system) or the "feeder" pores. Carbon dioxide adsorption at 298°K (DUBININ-POLANYI approach) is used to estimate specific surface area in all pores including the micropores, which closely approximate the total surface area. Maru and Lu[9] have carried out both types of measurements on commercial cokes and a formed coke. They also reported the increase of specific area due to oxidation and the decrease due to thermal treatment. A third method, much more convenient but less quantitative, by moisture absorption in the presence of water in a dessicator at room temperatures, has been evaluated. The corelations between moisture gain and specific surface area measured by carbon dioxide adsorption are given in Fig. 25[9].

(a) Specific Surface by the Adsorption of Nitrogen

There is an automated BET apparatus used for the characterization of mineral matters by our ceramics research group. Four types of specimens were investigated with this instrument and the results are given in Table 11.

Table 11 Specific Surface area by BET Method*, and reactivity.

Coke Samples	Specific Surface m^2/gm	Reactivity %/hr
As Received:		
Al-1	0.43	3.23
Al-2	0.57	2.15
Al-3	0.30	9.00
Re-1	0.40	4.16
After Oxidation by CO_2:		
Al-1 (13%)	8.05	3.23
Al-2 (14%)	3.15	2.15
Al-3 (27.4%)	36.83	9.00
Re-1 (16.2%)	11.07	4.16
After Potassium Absorption:		
Al-1 (6.7%)	0.47	
Al-2 (7.0%)	0.56	
Al-3 (6.8%)	0.28	
Re-1 (4.4%)	1.15	
Al-1 After Potassium Absorption (3.3%) and then Oxidation (27%)	1.42	17.20

*Surface Area Analyzer made by Micromeritics

Since this apparatus was not designed for carbonaceous materials, results shown in Table 11 must be checked. Three Swedish cokes were used for comparison and results are given in Table 12.

Table 12 Specific surface area by BET Method, and reactivity.

Coke Samples	Reactivity*	BET		Moisture Absorption
		McMaster	CANMET**	
MET	9.43	0.26	0.58	1.2
SSAB 1350	12.22	0.34	0.52	1.2
S.R.	16.19	0.96	1.46	1.7

* % Burn-off at 950°C in Ar-40% CO_2.
** The apparatus in the CANMET laboratory has more favourable conditions for desorption in a vacuum and a longer time for adsorption.

(b) Moisture Absorption

In order to compare data given in Table 11, this same set of coke samples was also investigated by the moisture absorption methods. The results are plotted in Fig. 26. Coke Al-3 has an area about three to four times larger than that of the other three cokes, as received as well as after oxidation by about 20% burn-off. Thermal treatment reduced the specific surface, particularly for Al-3. After the impregnation of potassium the ability of the coke sample to absorb moisture increases by one order of magnitude. It must be pointed out that a certain amount of water may be used to form potassium hydroxide and this would cause an error in surface area estimation.

Fig. 27 provides a different type of information from moisture absorption data. It illustrates the relative rates of moisture pick-up (in relation to samples of cokes as received). Partial oxidation of carbon by CO_2 allows the remaining coke samples, except Al-2, to more easily absorb moisture. Thermal treatment has the opposite effect, except on Re-1. Potassium in coke increases the rate and the amount of moisture gain by one order of magnitude.

10. Metallographic Examination

Specimens, as received and after various treatments shown in above sections were examined, under optical microscope as well as SEM. The results may be summarized as follows:

1. There are two types of surfaces, namely, fracture surface which was part of pore wall and pore surface.
2. The fracture surface is much more reactive for carbon dioxide oxidation.
3. Potassium absorbed in coke accelerates the oxidation of both types of carbon surfaces.
4. With enough potassium in coke, the difference in these two types of surfaces becomes much less significant.
5. On a given type of surface (fracture or pore) and within the domain of a given carbon form, the chemical property of carbon is not uniform in terms of oxidation by carbon dioxide.
6. Preferential orientation of "layer structure" of carbon frequently occurs adjacent to internal surface of pores.

11. Discussions

(a) The selectivity and kinetics of potassium absorption

It is a separate project now. Mr. T.T. Le is carrying out his M.Eng. thesis work on this topic. It is being supported by an operating grant from NSERC. The apparatus for potassium vapour generation and absorption is being improved to give better control of experimental conditions. Under SEM, one could observe the growth of a new solid phase on the surface of particles. The change of optical texture composition due to the absorption of potassium observed in the present work may be corresponding to this phenomenon. Polished surfaces of coke will be used for this type of metallographic investigation.

(b) The selectivity and kinetics of oxidation by carbon dioxide

To a certain extent, it was a disappointment for not being able to correlate reactivity of specimens investigated and its composition of carbon forms based on optical texture analysis as we did (5) and in literature (1,2, 6). Quantitative microscopy work were also carried at CANMET for confirmation on a few specimens and composition data are given in Table 13. However, present work led us to the following important preliminary conclusions:

(i) In each set of specimens we investigated, the major variable is carbonization conditions not the rank of coal, as in the literature.

(ii) Based on SEM observation of partially oxidized specimens, we observed similar results as reported by Marsh and Mochida (10). Isotropic carbon appears to be more reactive uniformly in the entire areas. The gasification of anisotropic carbons (mosaic, granular and flow-types) are highly non-uniform in each domain. This type of heterogeneity may be partly caused by the orientation of basal plane and prismatic edges at the surface. It may suggest that the composition of carbon forms may not be the proper parameter in terms which assess or predict reactivity.

(iii) In the boundary region where two domains of different carbon forms meet, the carbon is more reactive to carbon dioxide.

(iv) The isotropic carbon and carbon in the boundary regions which are more reactive, may simply have higher internal specific surface area and are more accessible to the oxidizing gas.

(c) Specific surface area of Cokes

Our preliminary results are given in Tables 11 and 12 and Figs. 26 and 27. The specific surface area of partially oxidized specimens and that of Swedish origin measured with a simple BET apparatus at McMaster, correlates qualitatively very well with reactivity (Table 4). On the other hand, the moisture absorption data (an estimate of surface area may include much finer pores than BET measurement) detects the unusual reactivity of specimen A1-3 very clearly. The change in the kinetics of moisture gain, Fig. 27, also shows clearly the change in the openness of the pore structure.

Jenkins et al (3) and Maru and Lu (9) have attempted to find a relationship between reactivity and specific surface areas. With single-coal chars or cokes, specimens of varying specific surface area by both N_2 and CO_2 adsorption were prepared by various heat treatment temperatures up to 1000°C(3). The area measured by N_2 adsorption correlates better with reactivity than the surface area by CO_2 adsorption. Jenkins et al. (3) suggested that the combination of pore structure (amount of feeder pore) and chemical nature of char or coke (hydrogen content) are the governing factors for reactivity. Heat treatment may lower the specific surface area and oxidation has the opposite effect. After a small degree of oxidation, the effect of heat treatment (in the lowering of the surface area) diminishes.(9) These data indicate different emphasis on N_2 and CO_2 adsorption surfaces.

(d) Practical Importance of Reactivity Data

The effect of size (from powders to lumps) on reactivity measurement has been and will be a topic of debate for some time to come. The possible causes for such diversity at least include the following:

Table 13 Comparison of measurements made in two laboratories on coke Re-1.

	CANMET					McMASTER				
	As-Received	Oxid. 25%	K Abs.	Thermal Treatment	K^+ Oxid.	As-Received	Oxid. 25%	K Abs.	Thermal Treatment	Oxid. 25%
Isotropic	0.0	0.0	0.0	0.0	0.0	0.3	1.6	0.3	1.0	2.0
Fine	5.4	4.5	7.6	7.4	2.4	3.3	0.3	0.3	0.7	0.0
Medium	25.4	24.5	42.2	36.8	31.9	1.3	1.0	0.0	0.7	0.0
Coarse	0.0	0.0	1.0	0.8	0.4	46.0	7.3	6.3	29.3	12.6
Elongated Flow	54.2	58.5	28.2	33.0	51.9	33.6	78.6	79.3	54.7	68.0
Domain(creased)	1.2	3.5	9.4	7.2	4.1	6.0	3.0	2.6	3.7	7.3
Domain(flat)	0.0	0.3	0.0	0.4	0.4	0.0	0.3	0.0	0.3	0.6
Ribbon	0.0	0.0	0.0	0.0	0.0	0.3	0.3	0.3	0.0	1.6
Inerts	13.8	8.7	11.6	14.4	8.9	9.0	7.3	10.6	8.7	7.6

Comments: 1. Approximately our medium mosaic at CANMET is coarse mosaic at McMaster.
2. Because a medium and coarse mosaic is close to elongated flow (a "value judgement" is required about length to width ratio) both sets of readings swing strongly from one to the other, but for different samples.
3. The general conclusion at CANMET is that neither of the two laboratories have found significant changes from one sample to the next. BUT the amount of inerts in the oxidized samples may be less. Should repeat on 3 or 4 more samples to confirm.

(i) Diffusional effect of gaseous reactant and product (11).

(ii) Difference in fracture and pore surfaces.

(iii) Effects of fissuring on strength.

Lu et al. (5) have reported a general relationship that for several kinds of cokes and under various experimental conditions, the lowering of strength of discs only depends on the degree of gasification of carbon. Chiu (6) investigated the After-Reaction-Strength of coke (of course, the reactivity) with specimen initially of 20 mm size. From his data, Figs. 28 and 29 are prepared. It shows that higher reactivity leads to lower strength after reaction is very clear. The correlation between CSR (coke strength after reaction) and blast furnace performance has been reported. (12).

12. SUMMARY

1. The main task of this project is to investigate possible relationships between the chemical reactivity of coke, with respect to carbon dioxide, and its structural parameters, with and without the contribution of potassium in coke. Coke samples were obtained from two Canadian steel companies and one U.S. source. Cokes from each supplier are different mainly in carbonization conditions rather than the make-up of coals in the blends.

2. The selectivity of oxidation by CO_2 among different carbon forms in these cokes were investigated extensively by quantitative analysis of optical texture. Other than that the inerts are more reactive, no pronounced pattern could be conclusively identified.

3. The reactivity of cokes investigated was found closely related to specific surface area which was estimated by moisture absorption. The larger the specific surface area the larger the reactivity of the coke is. It is certainly consistent with the basic principle of heterogenous chemical kinetics.

4. A variety of conclusions have been reached by many authors that reactivity of coke depends on the rank of coals, forms of carbon, carbonization temperature, pore volume, etc. However, specific surface area is also dependent on these variables. It may be suggested that reactivity is proportional to accessible surface area and indirectly relates to other structural parameters through specific surface area. Coal properties and carbonization conditions of course, determine all structural parameters.

5. With respect to CO_2 oxidation, there are two types of surface in cokes investigated, i.e., fracture surface of pore wall and pore surface. Based on optical and SEM micrographs, the former is much more reactive than the latter. It would result in variation of reactivity when there is a change in size of particles in coke samples.

6. The effects of potassium absorption in coke are (a) an increase in specific surface area, and (b) making pore surface as reactive as fractural surface.

13. RECOMMENDATIONS

1. More elaborate and extensive surface measurement should be carried out and its relationship to reactivity established.

2. The relationship between specific surface area and coal blends, carbonization conditions, potassium absorption should be investigated.

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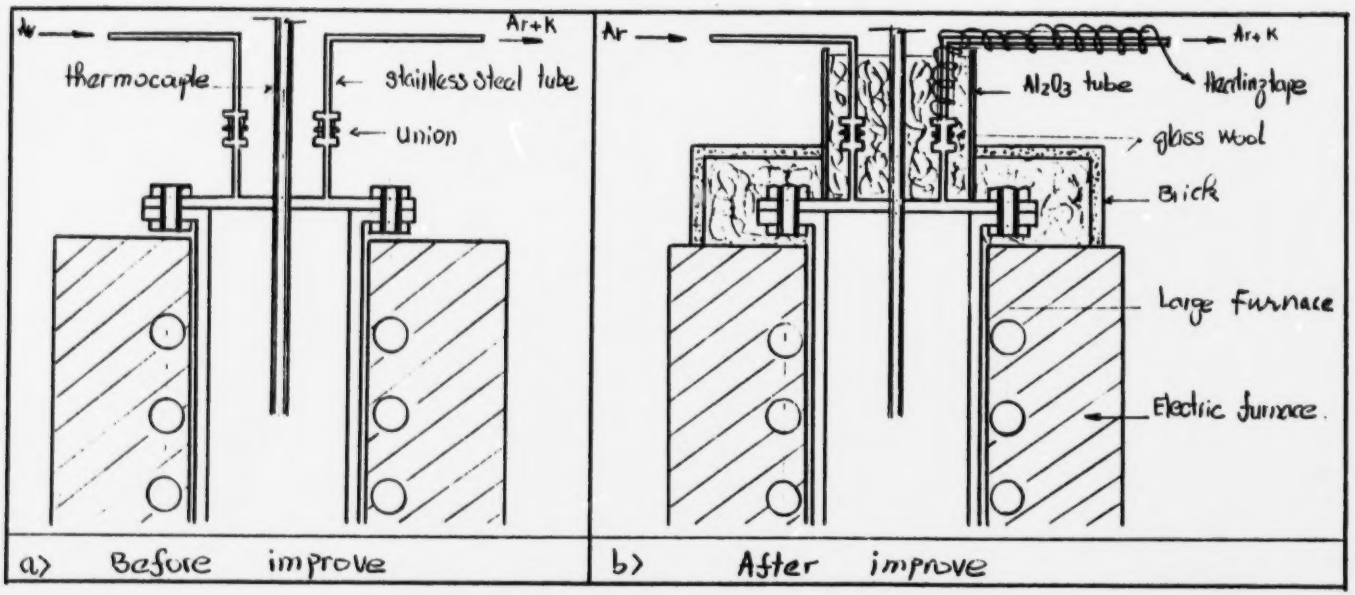


Fig. 1 Modification of alkali vapour generation and absorption furnace.

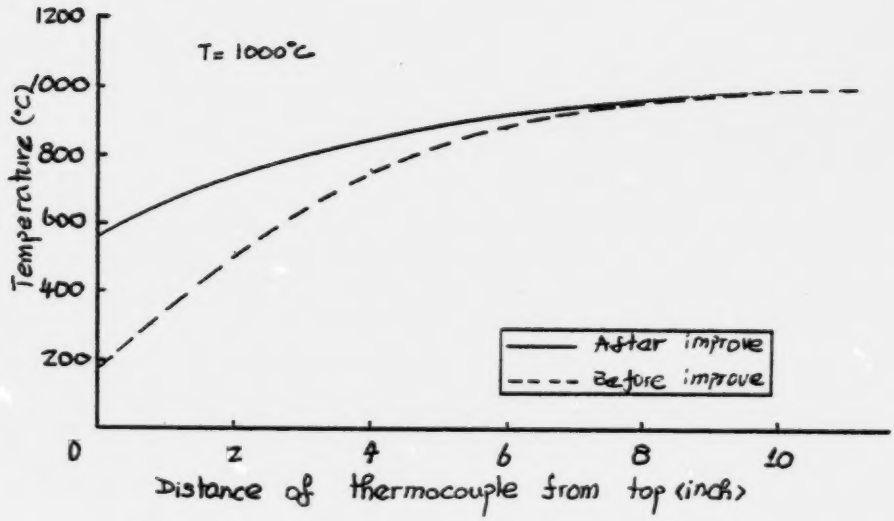


Fig. 2 Temperature profile in chamber for alkali absorption of carbon.

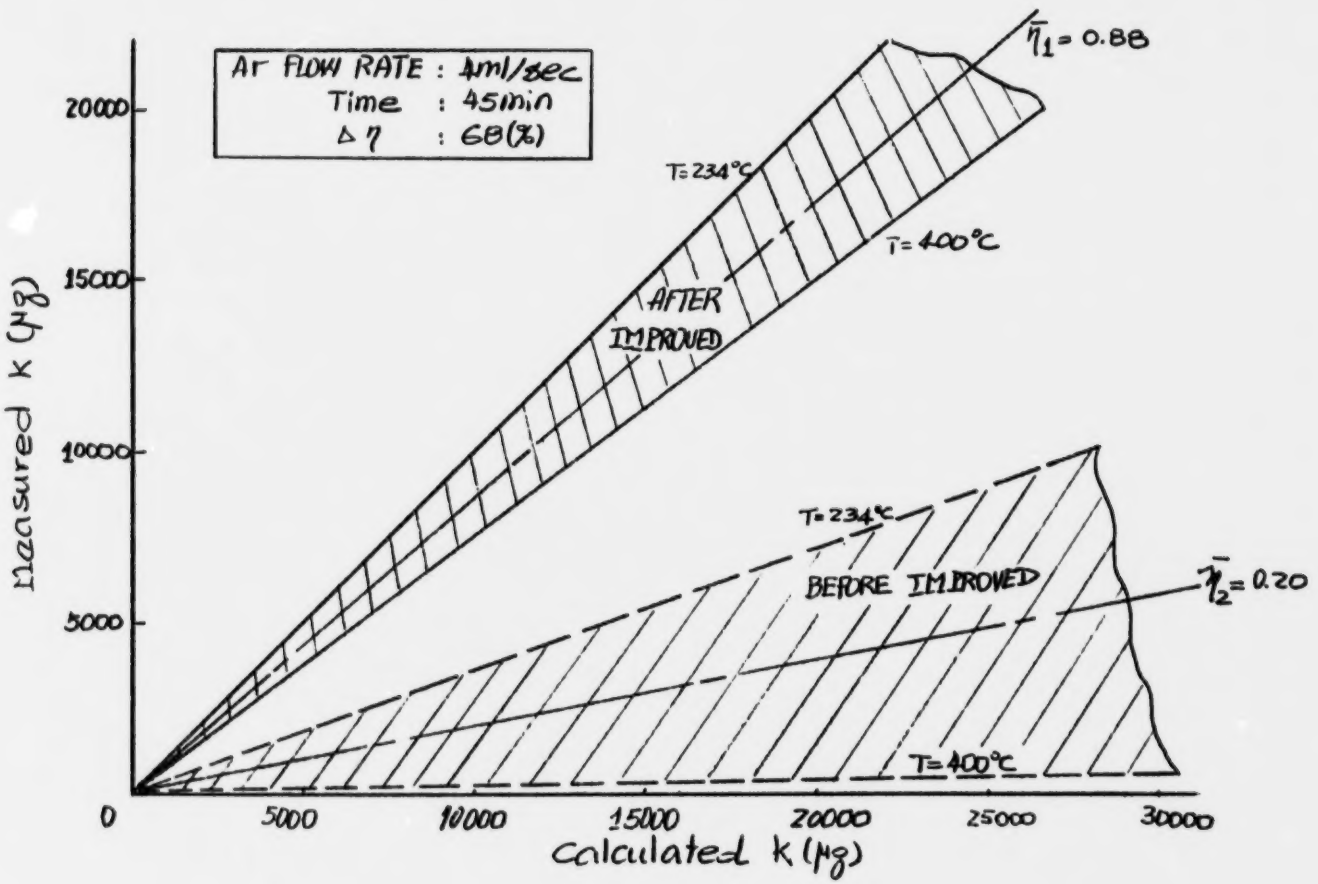


Fig. 3 Improvement in the control of alkali vapour pressure.

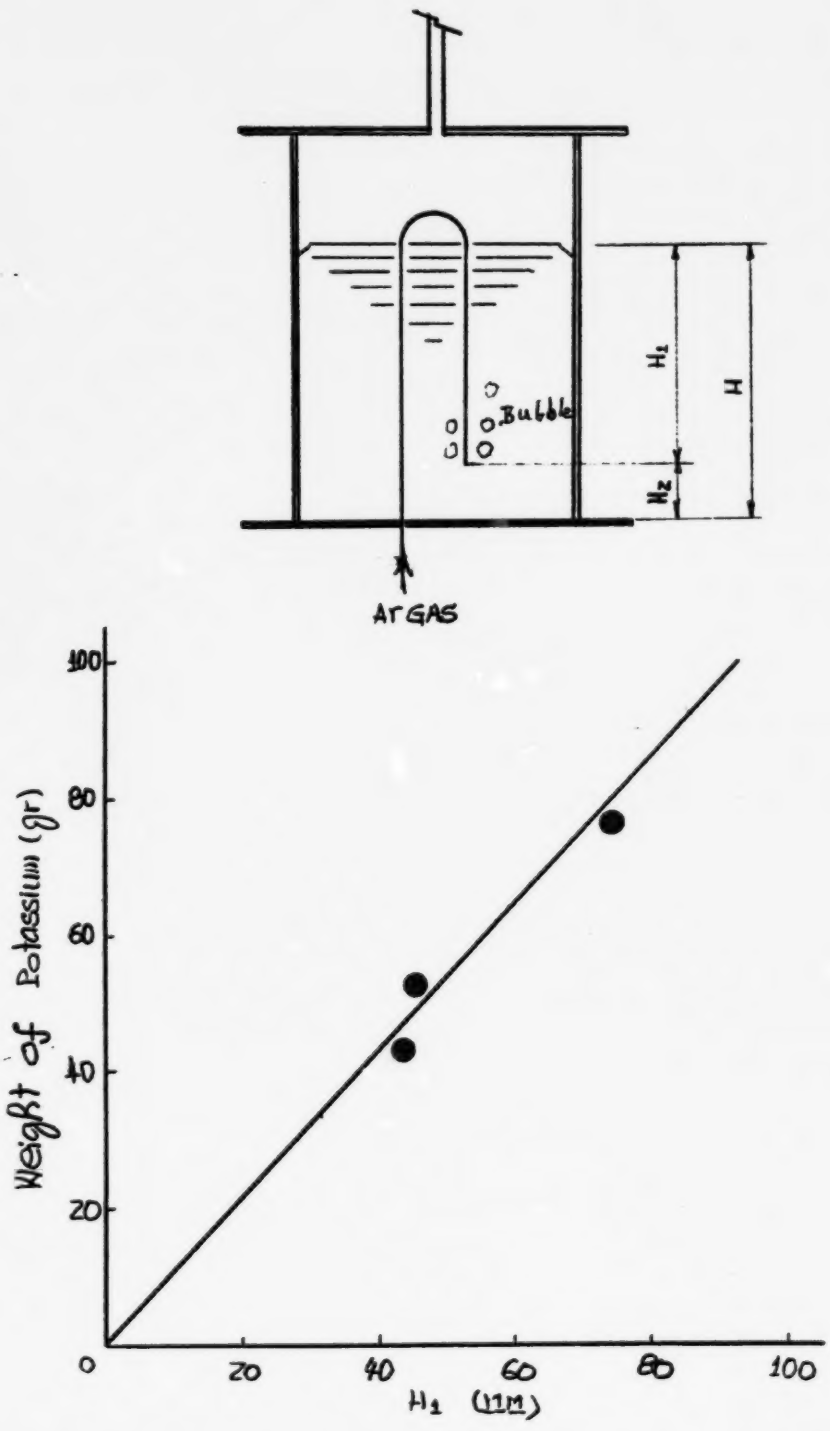


Fig. 4 The rate of potassium vapourization and the depth of the melt above the argon inlet.

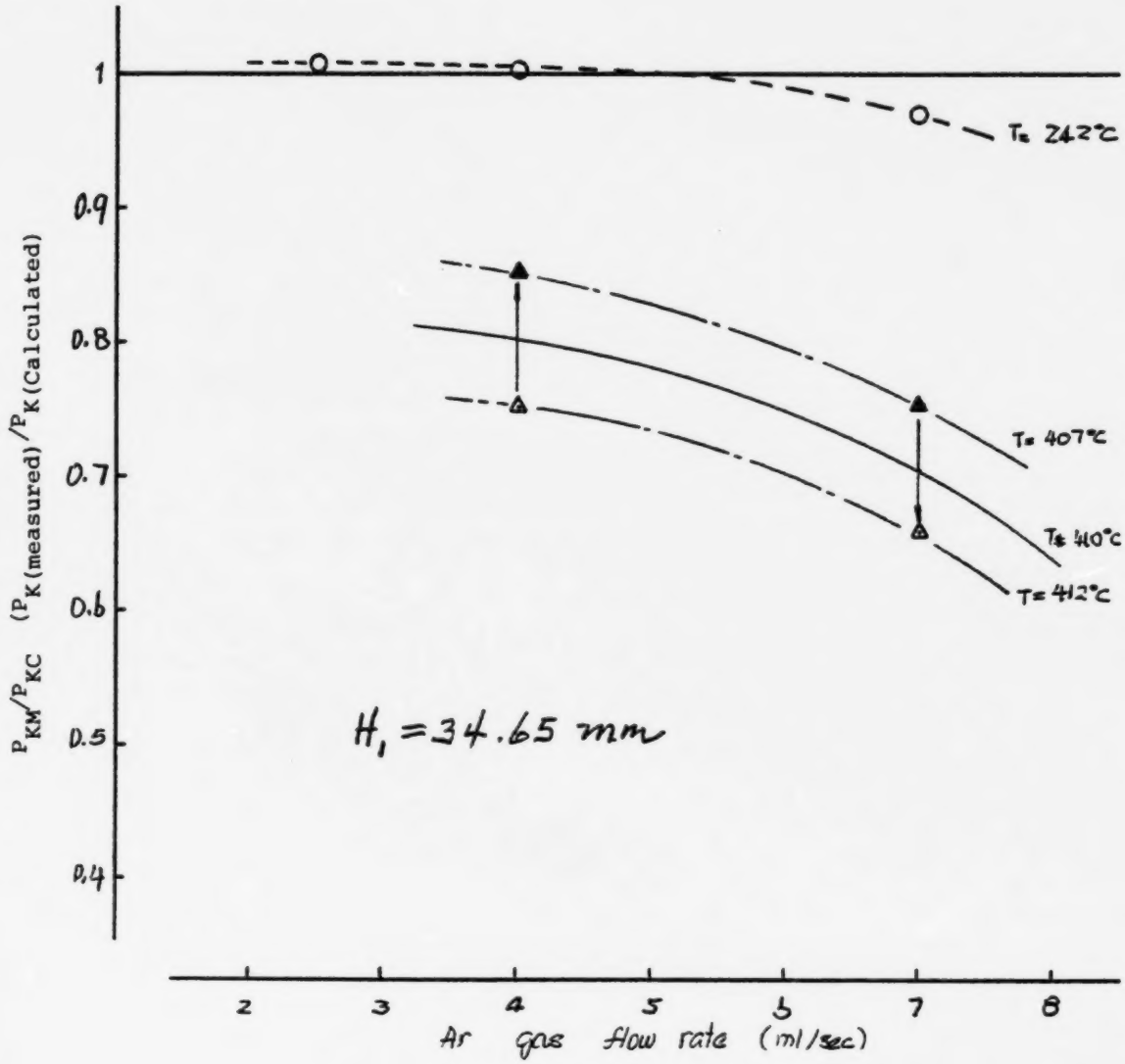


Fig. 5 The variation of potassium vapour pressure with temperature and argon flow rate, over a period of time in the range from 900 to 2700 seconds with shallow melts.

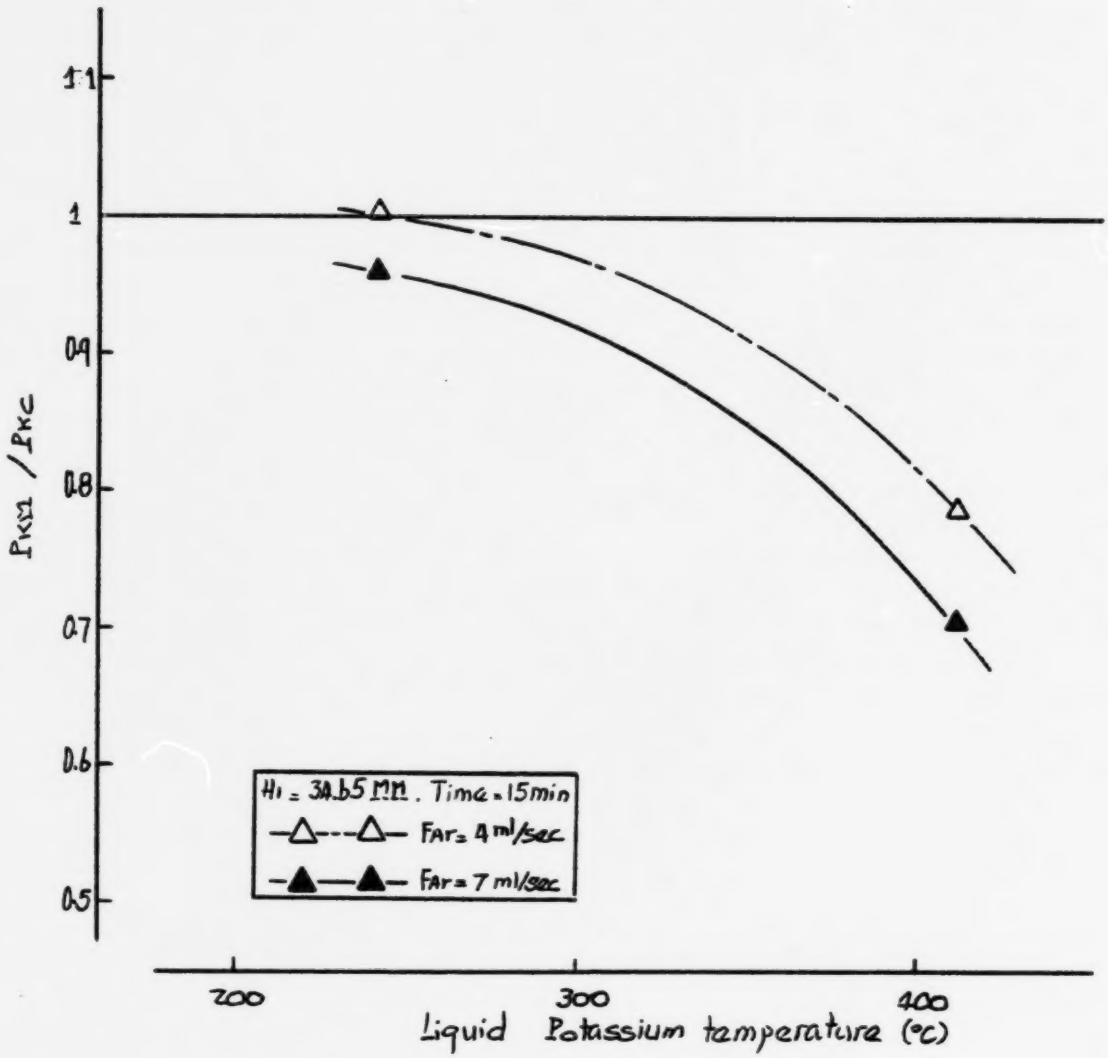


Fig. 6 The strong temperature dependence of potassium vapourization from the shallow melt.

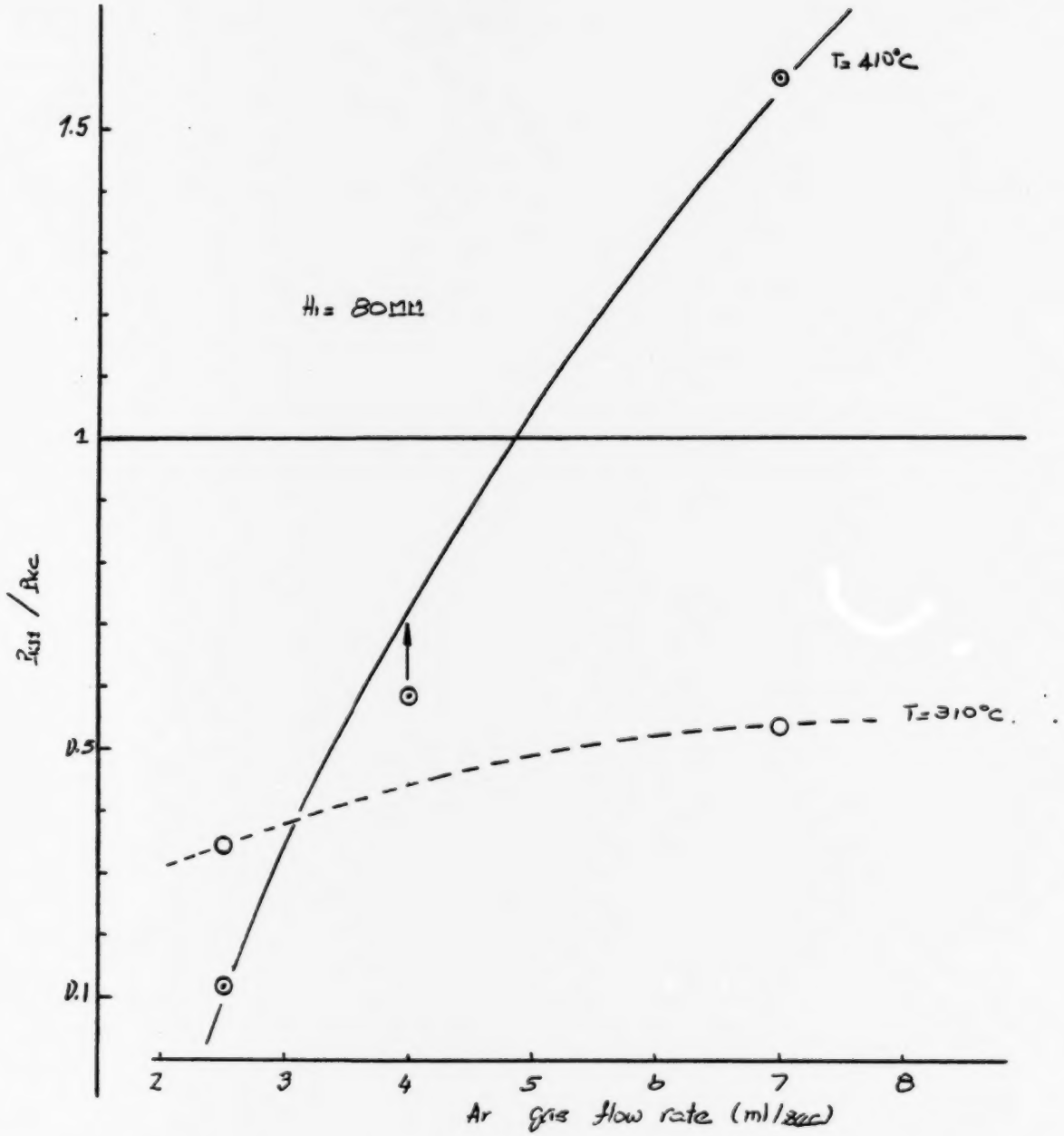


Fig. 7 The variation of potassium with temperature and argon flow rate from the deep melt.

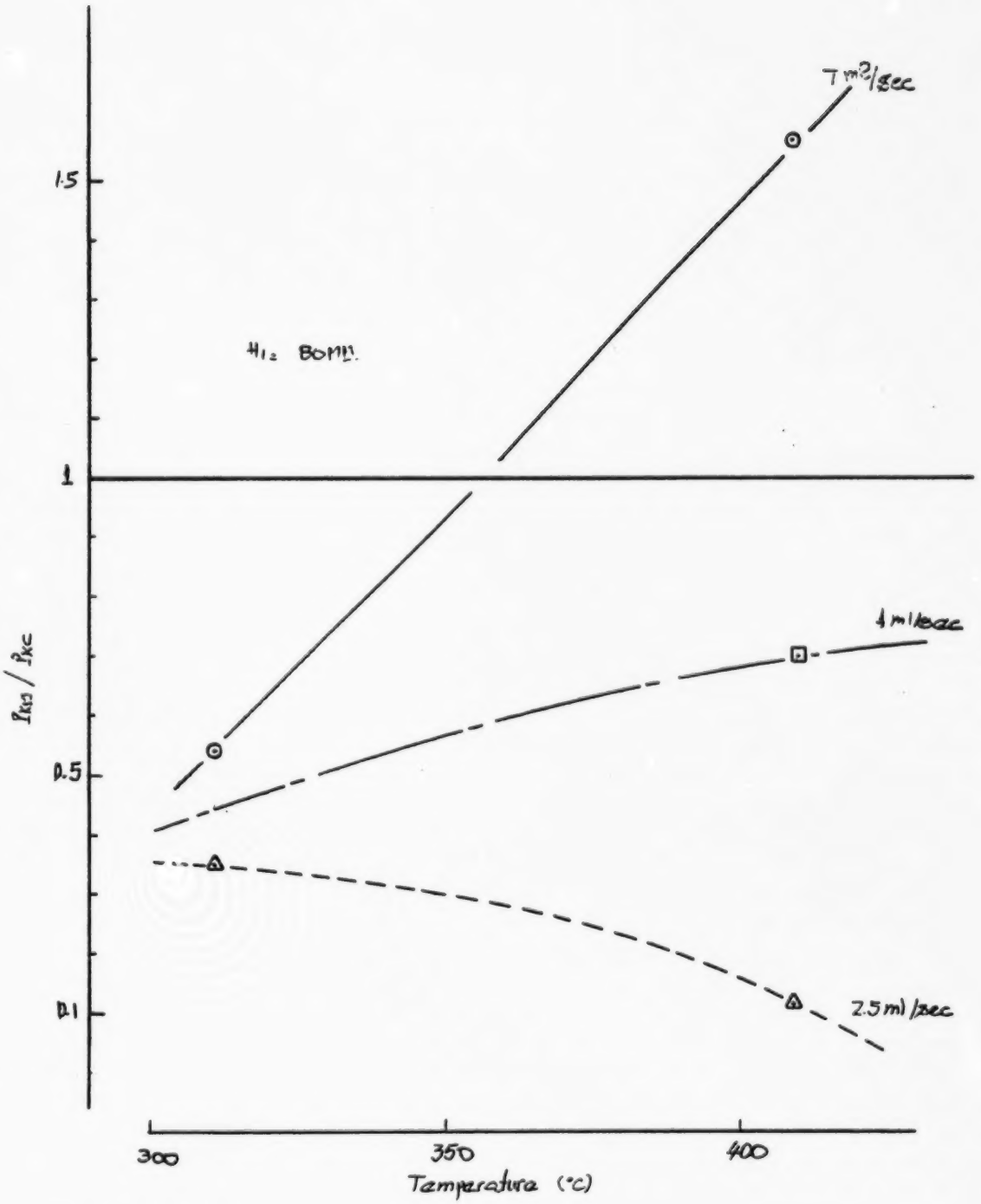


Fig. 8 The variation of potassium vapourization with temperature and argon flow rate from the deep melt.

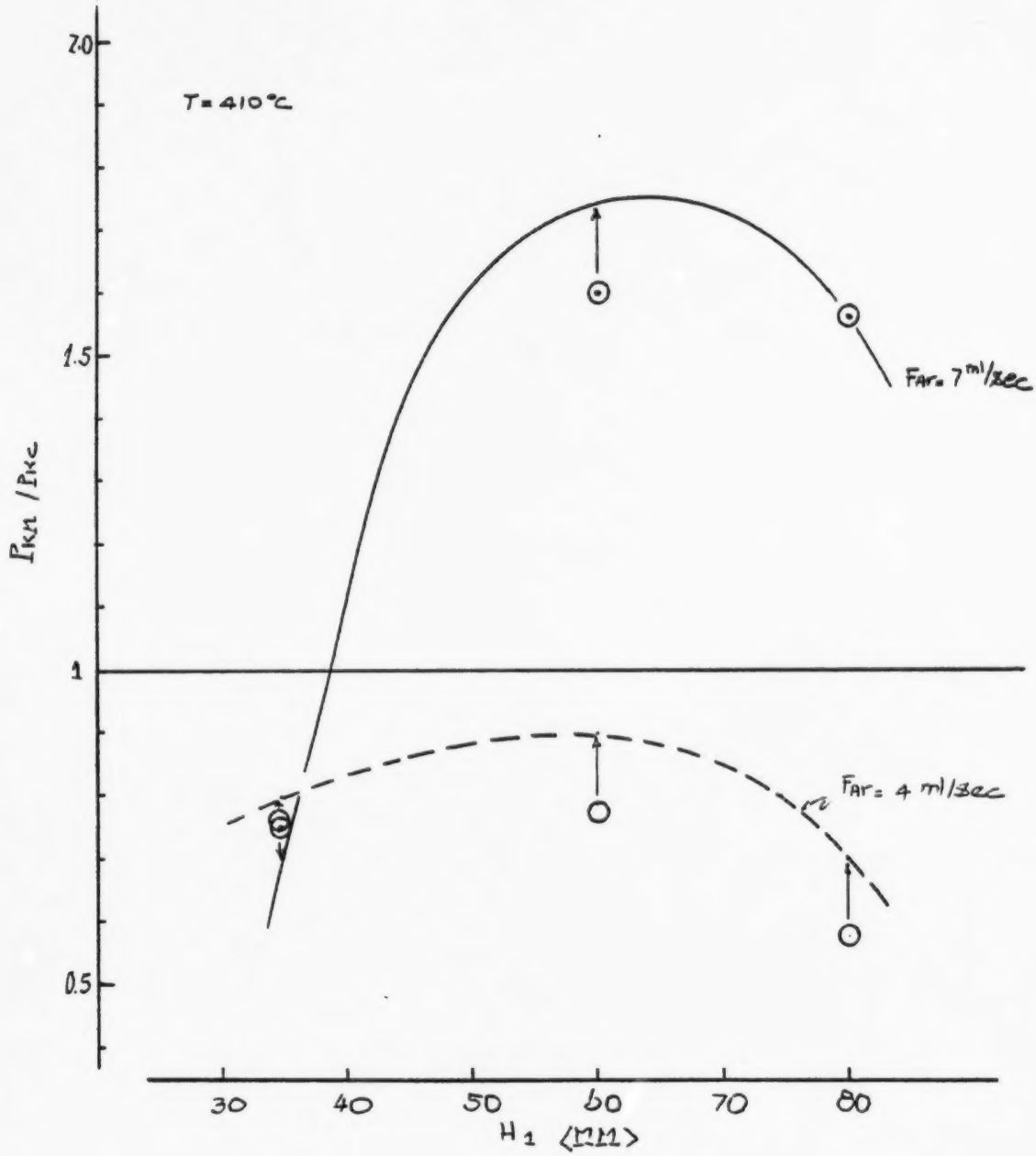


Fig. 9 The variation of potassium vapourization with the depth of the melt above the argon inlet.

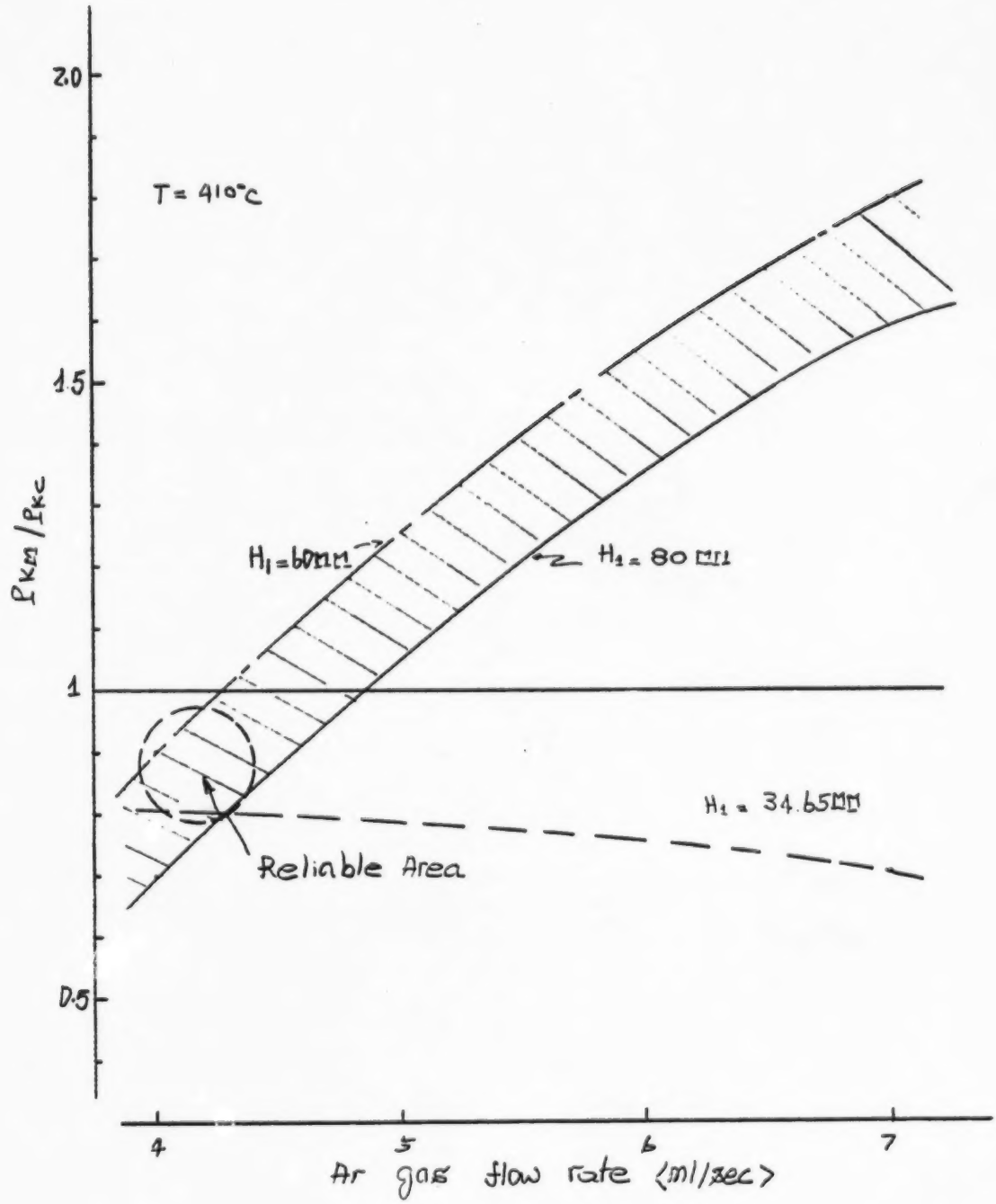


Fig. 10 Optimum experimental conditions for the preparation of Ar-K gaseous mixture at 410°C.

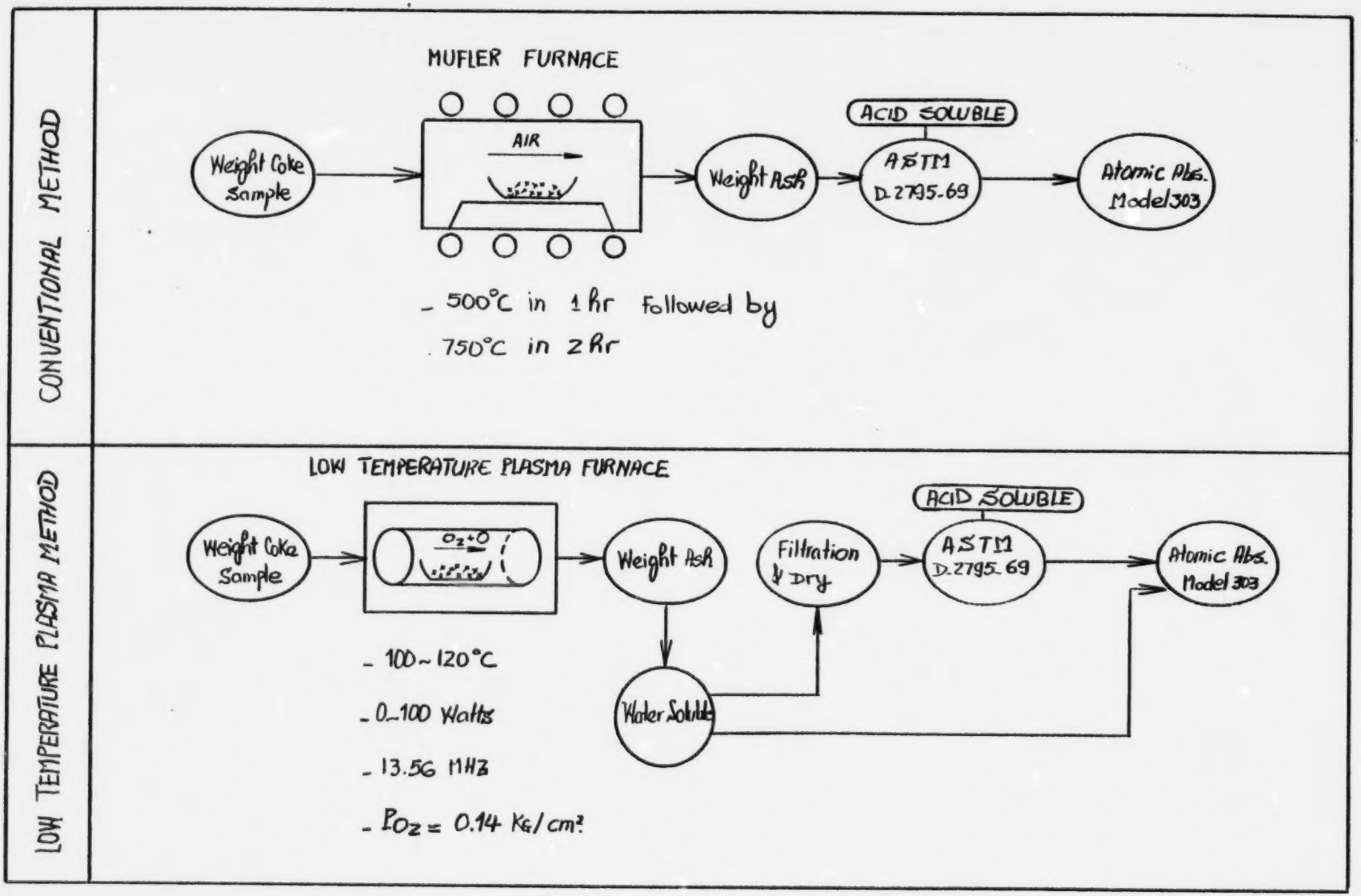


Fig. 11 Coke ashing procedures.

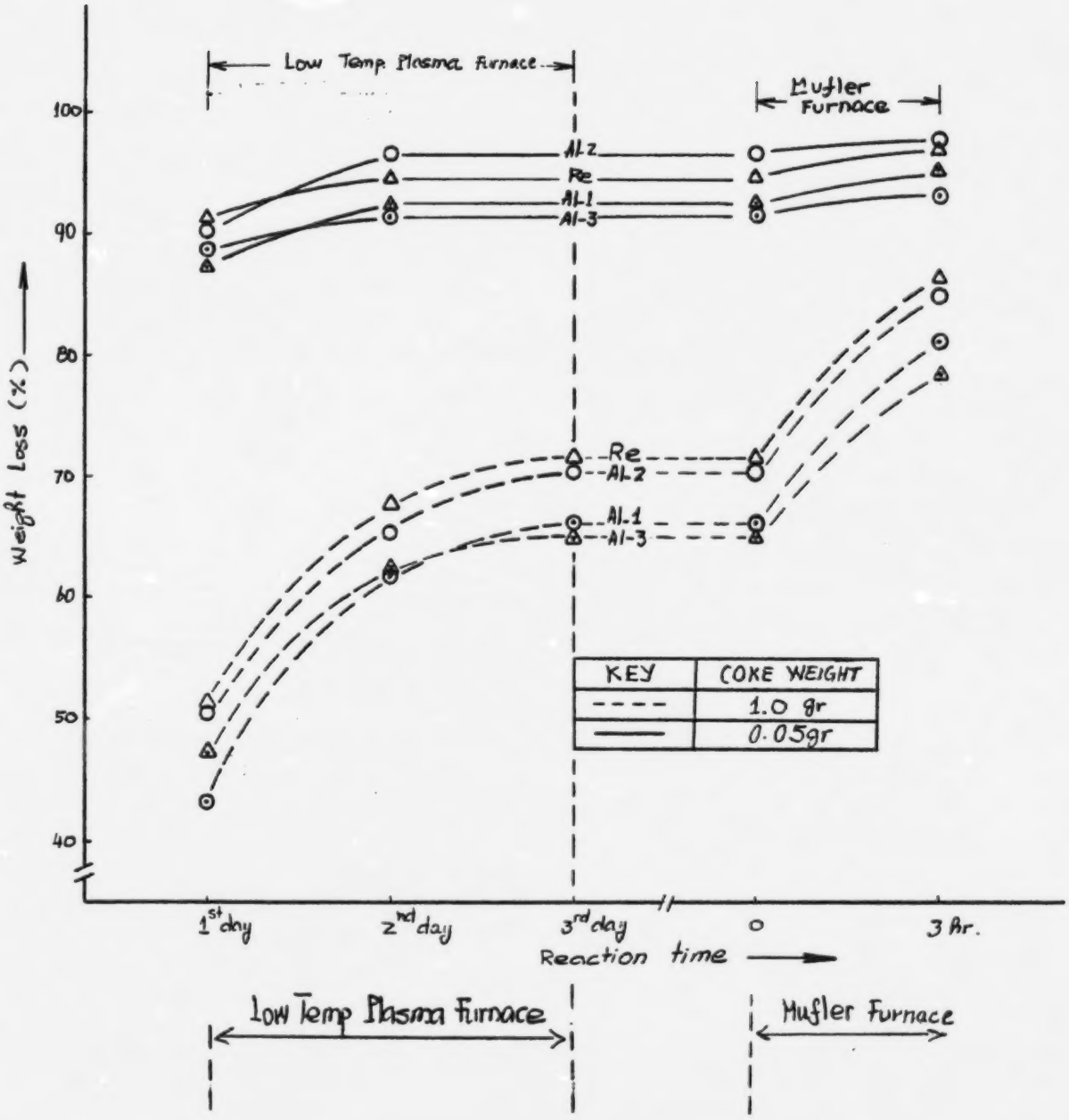


Fig. 12 Kinetics of gasification of carbon during ashing.

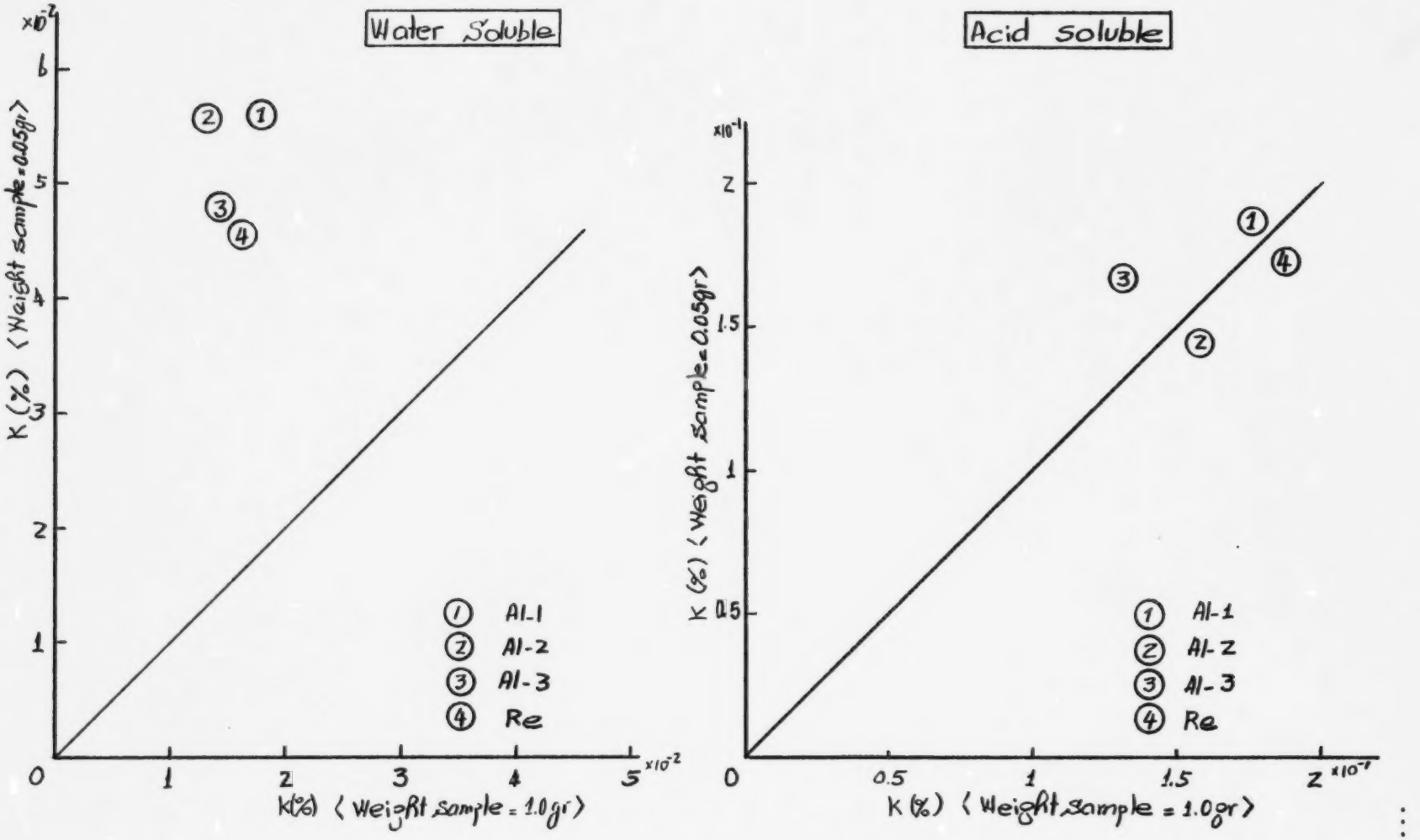


Fig. 13 The dependence of sample size of coke, with low temperature ashing, for potassium analysis.

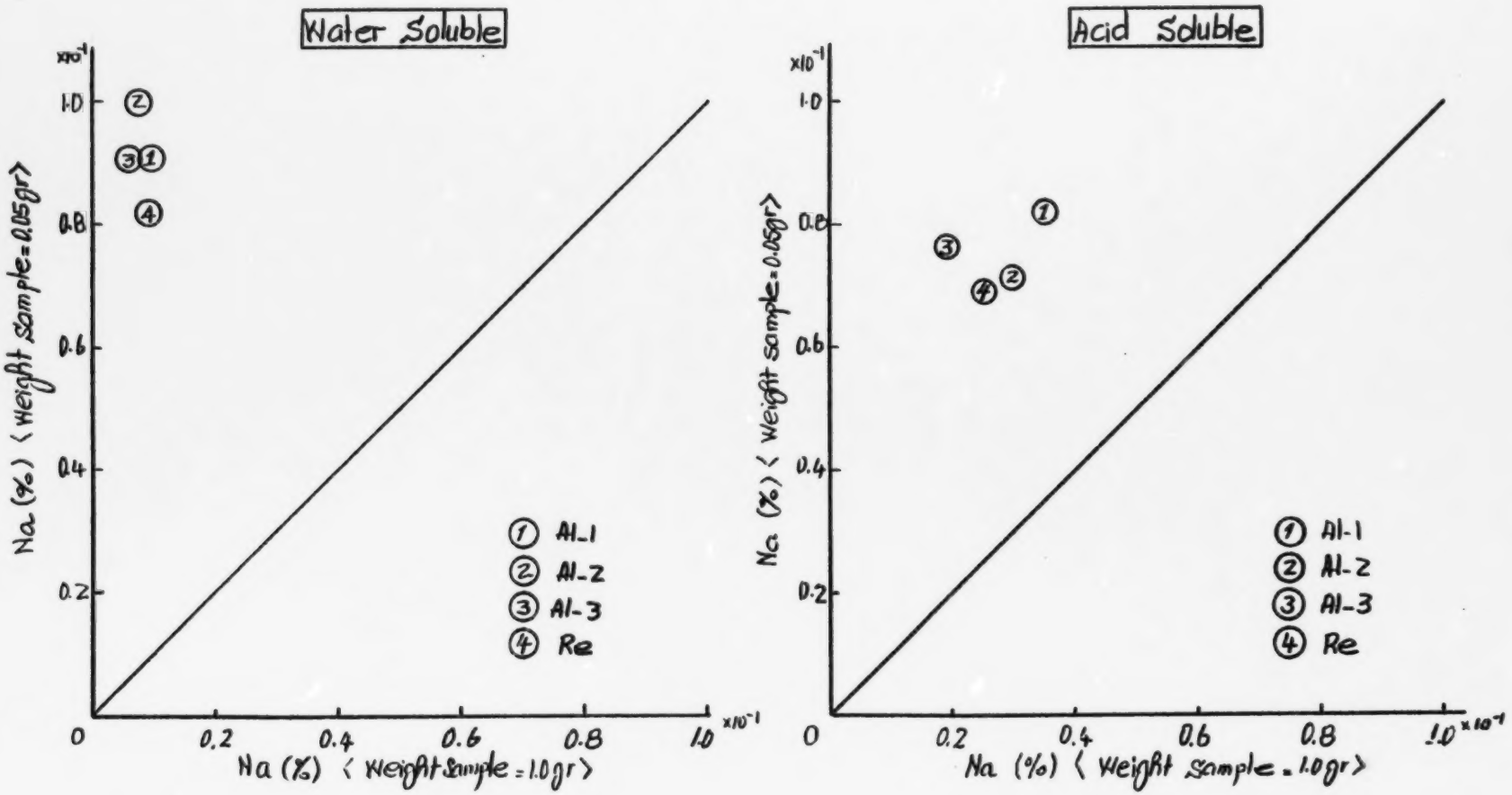


Fig. 14 The dependence of sample size of coke with low temperature ashing for sodium analysis.

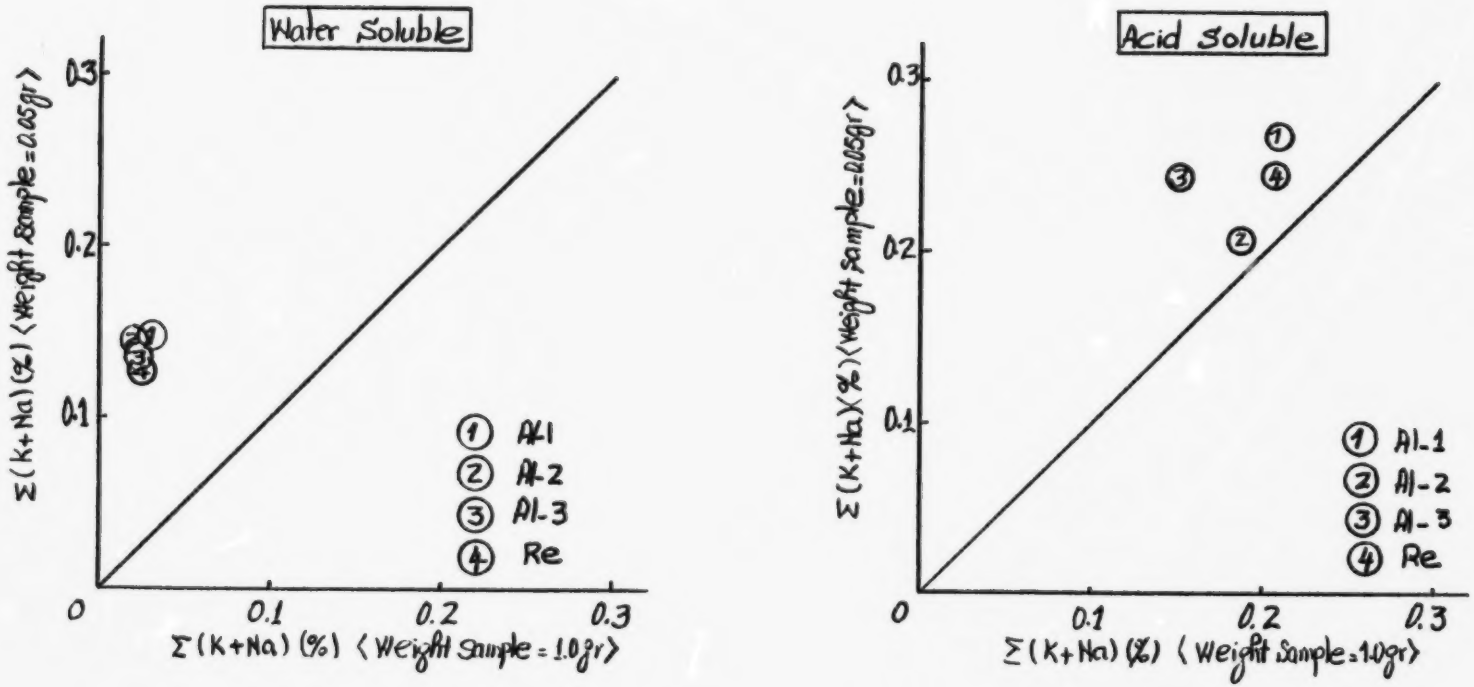


Fig. 15 The dependence of sample size of coke with low temperature ashing for alkali analysis.

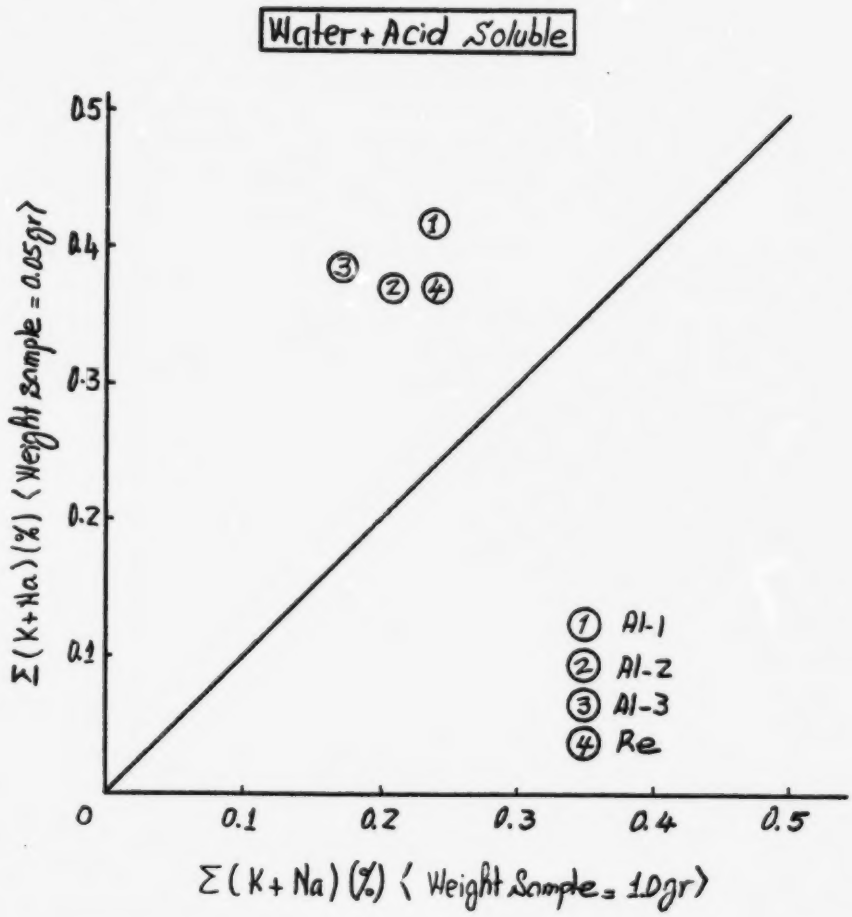


Fig. 16 The dependence of sample size of coke with low temperature ashing for total alkali analysis.

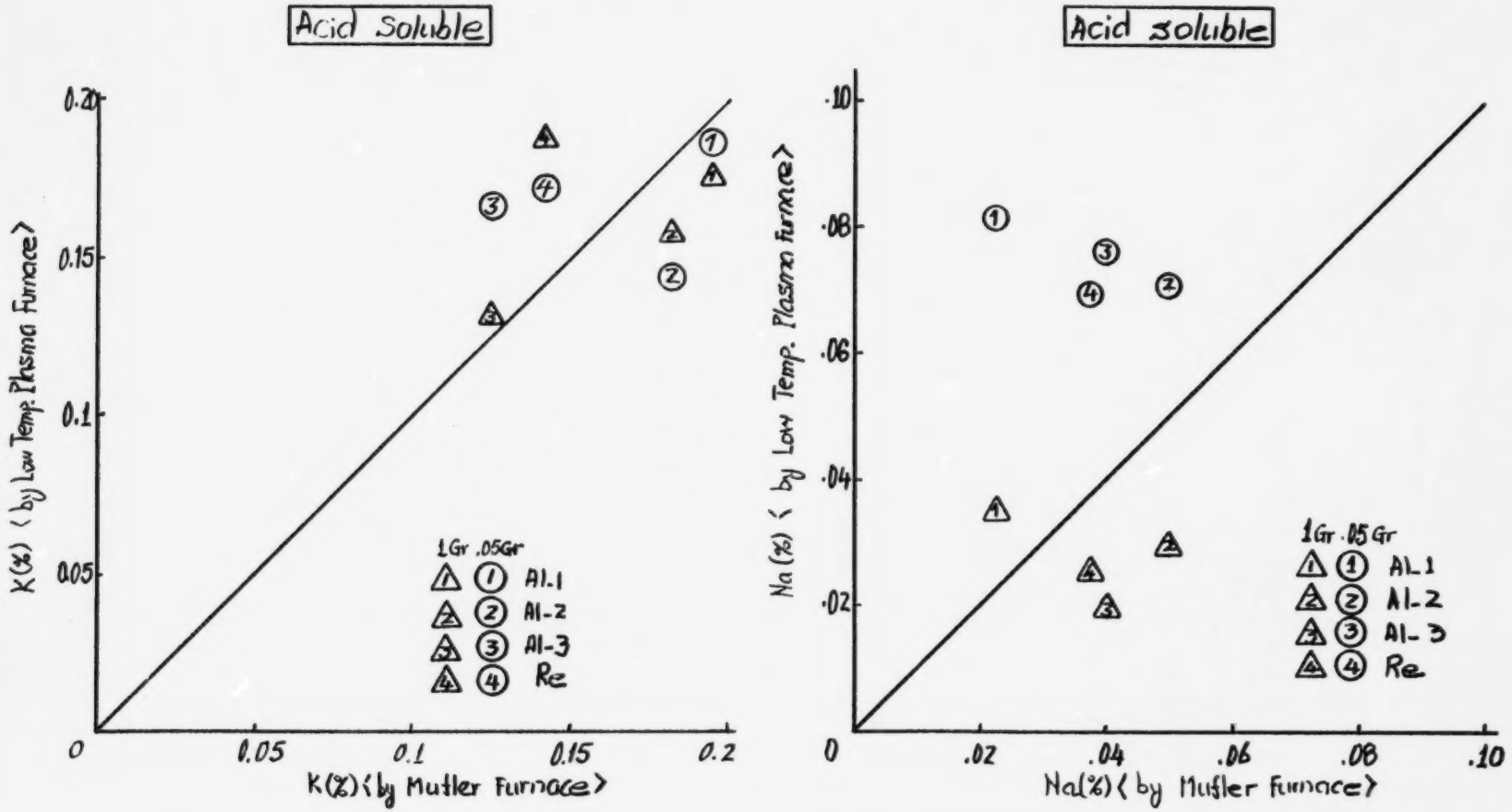


Fig. 17 Comparison of analytical results with and without low temperature ashing.

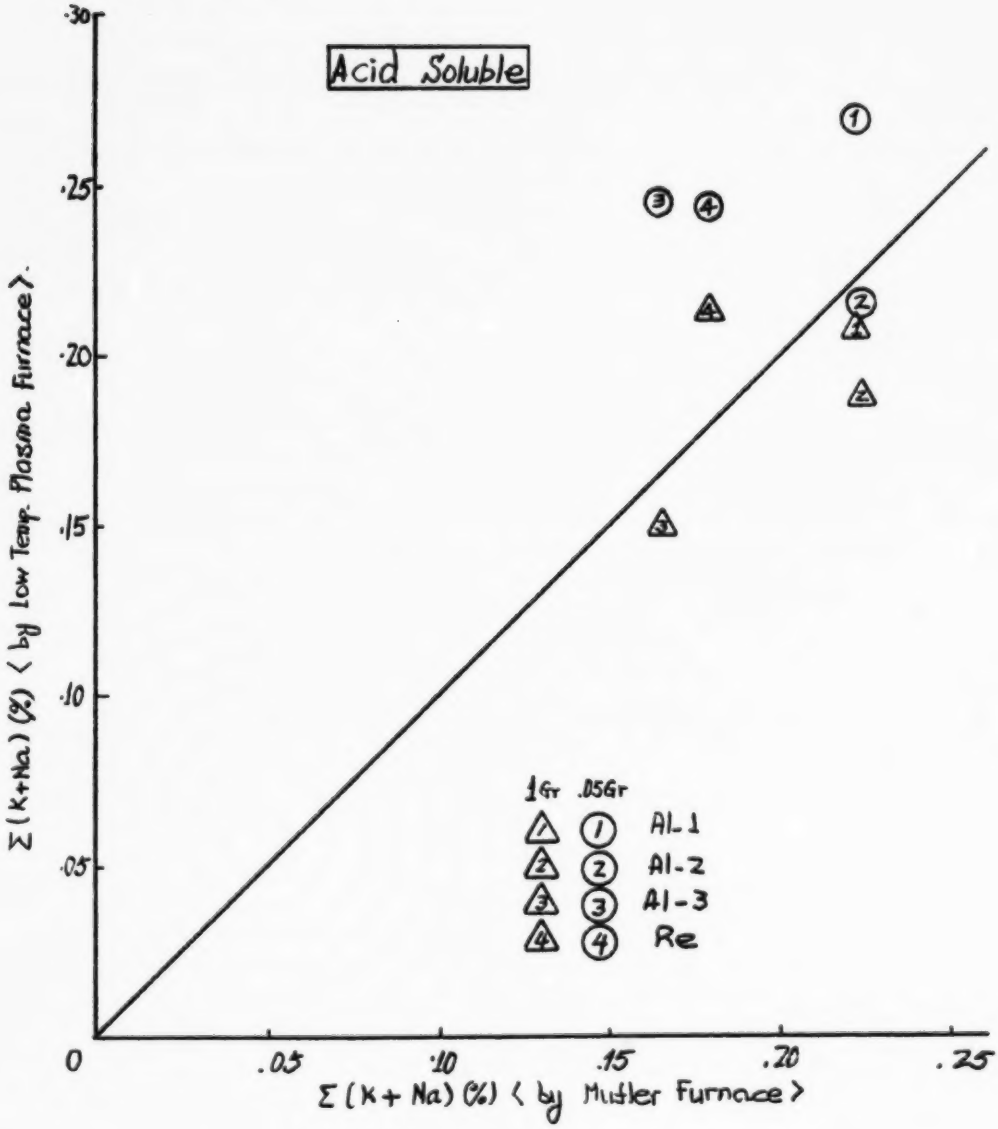


Fig. 18 Comparison of analytical results with and without low temperature ashing.

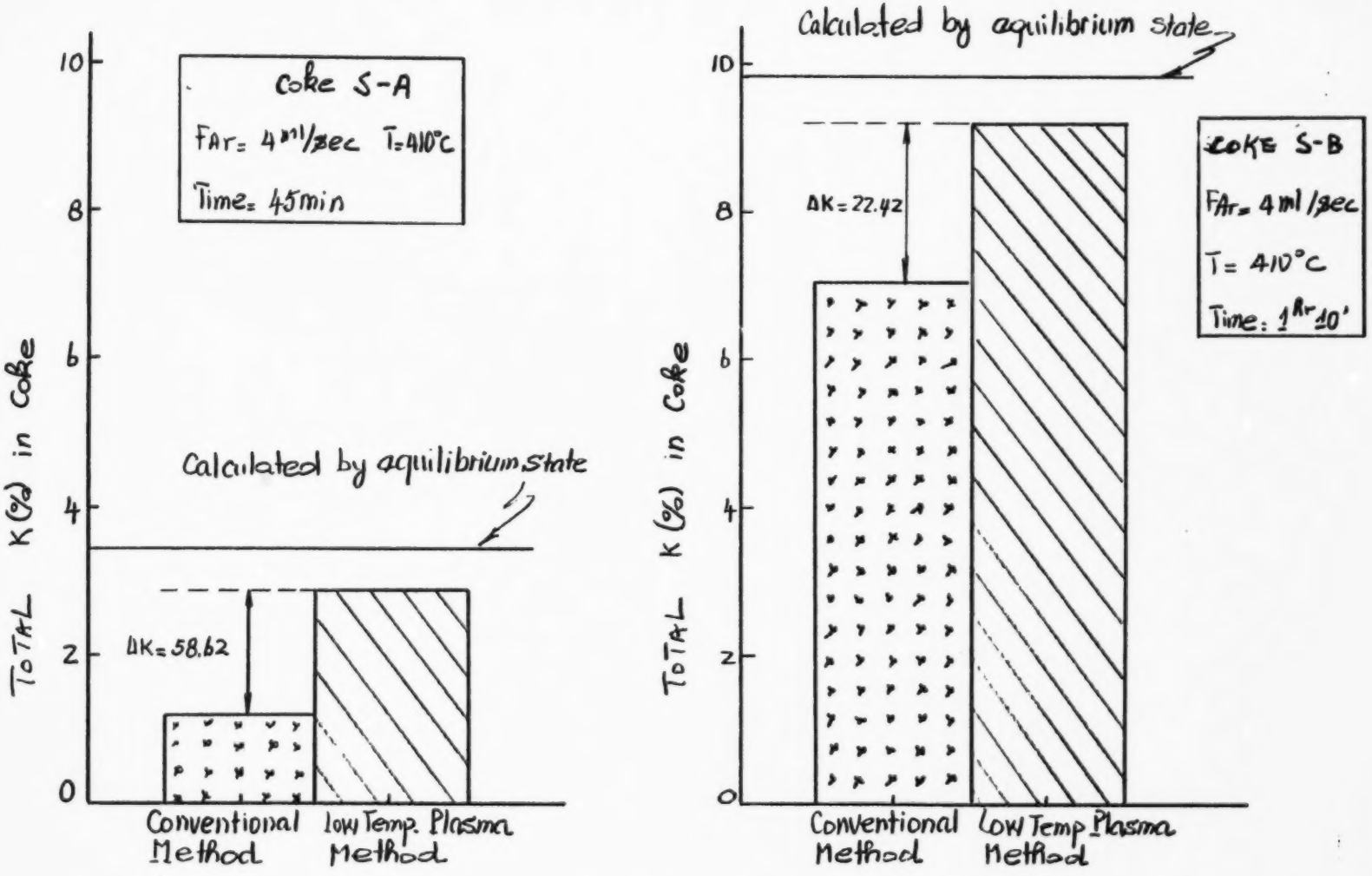


Fig. 19 Comparison of analytical results of two commercial cokes, with and without low temperature ashing, and calculated limits based on the amount of potassium available in the gaseous phase during absorption experiments.

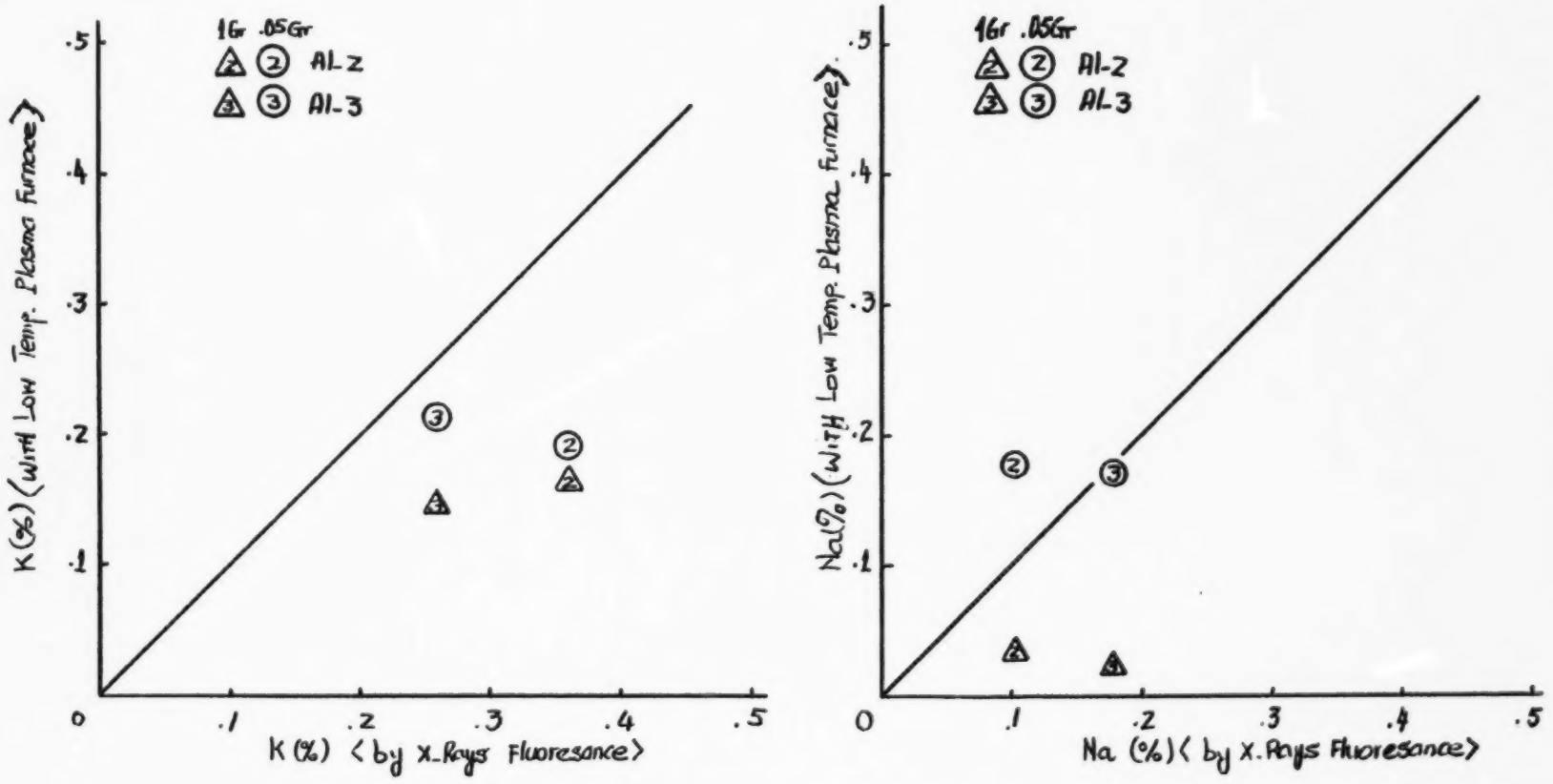
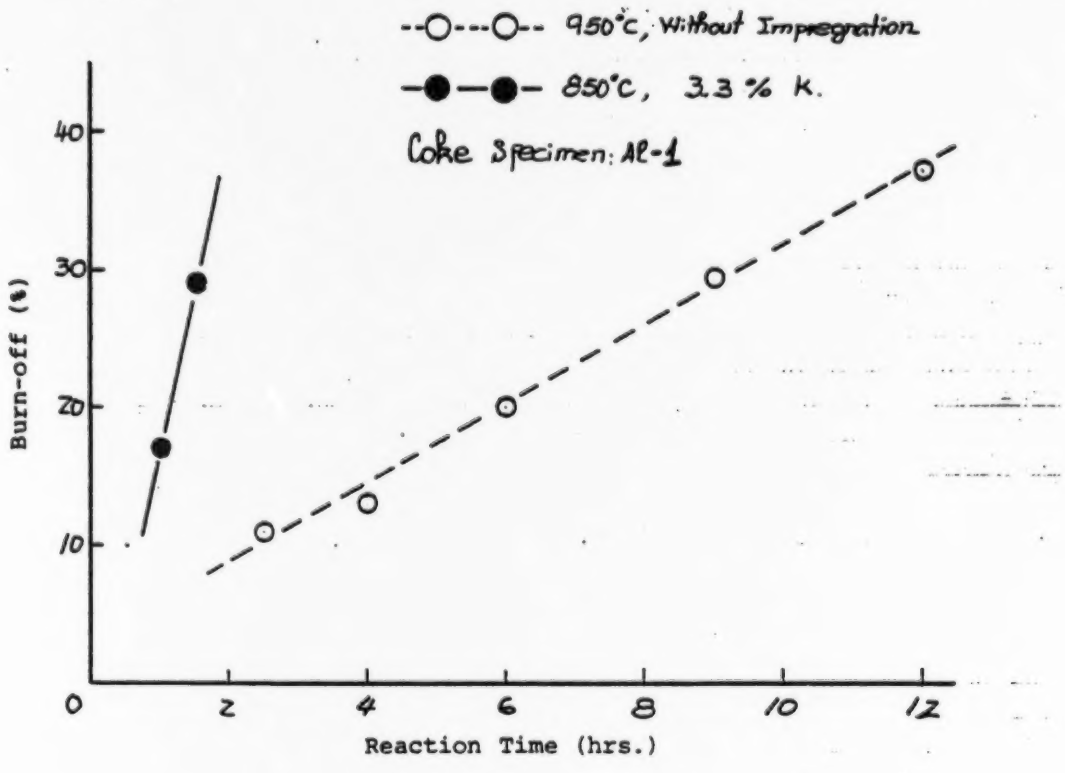


Fig. 20 Comparison of analytical results of total potassium and total sodium by x-ray fluorescence and by low and high temperature ashing.



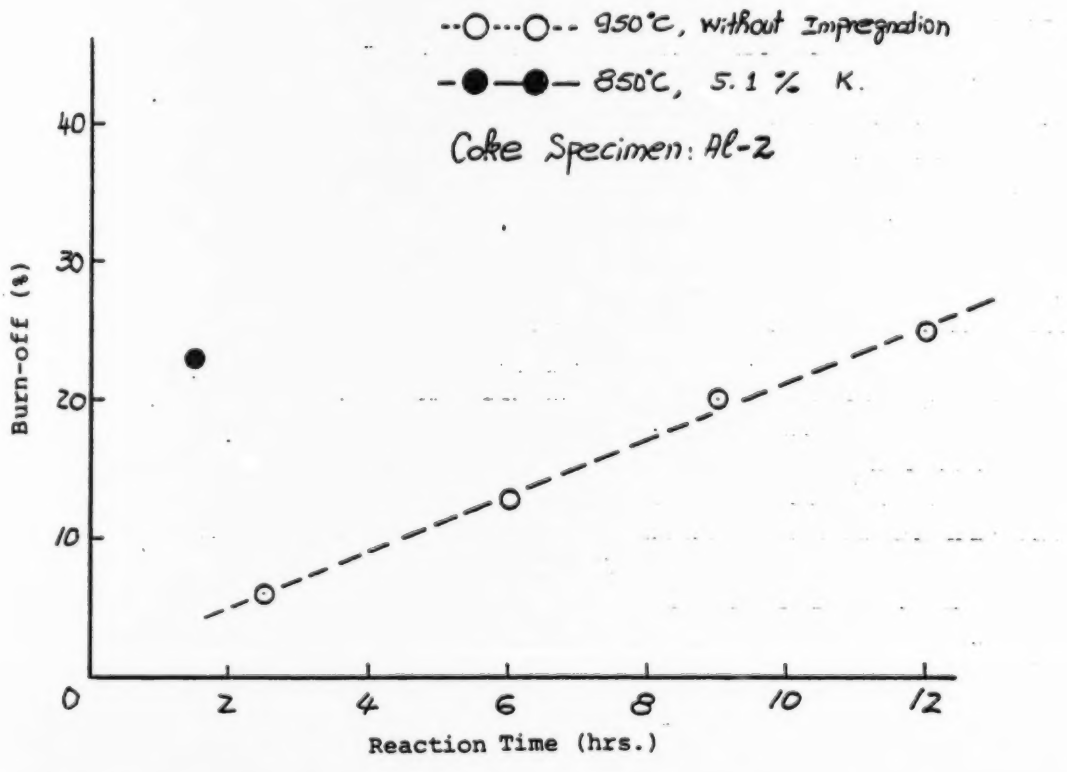
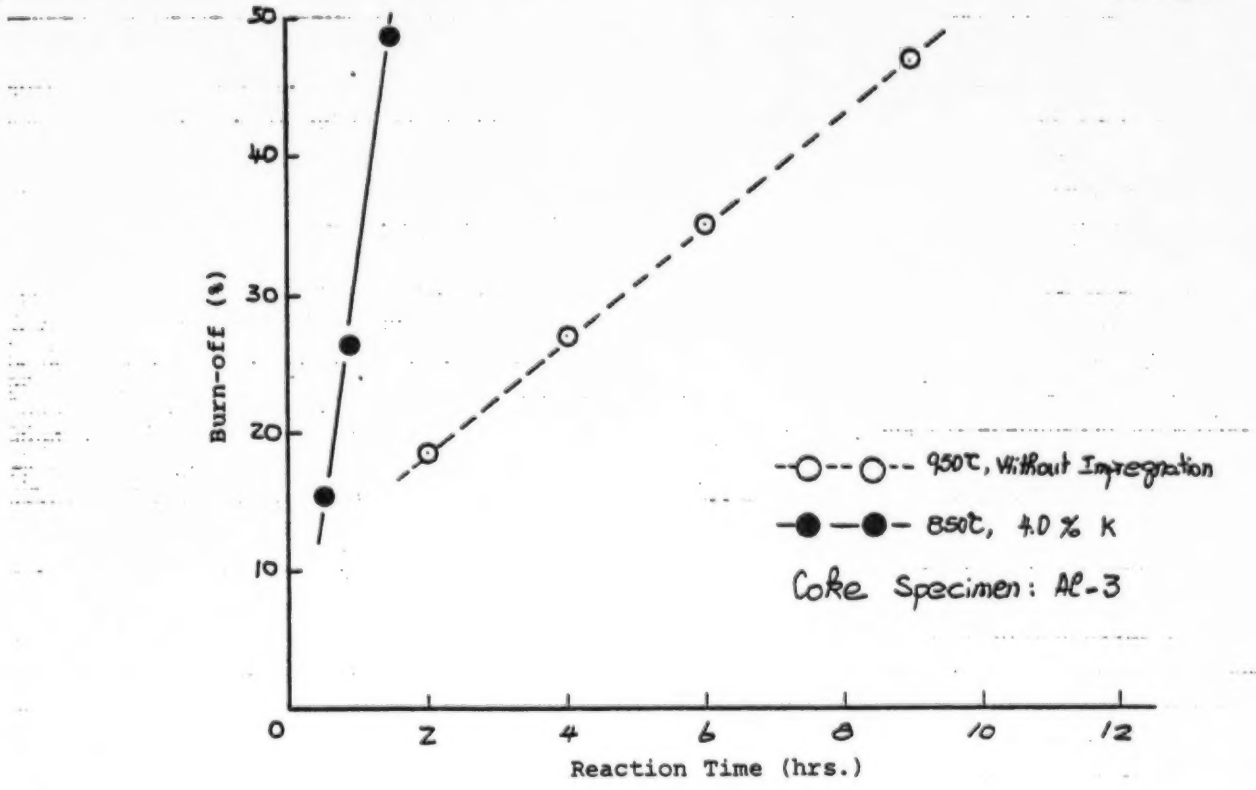


Fig. 21 Kinetics of oxidation of cokes Al-1 and Al-2 in $Ar/CO_2/CO$ mixture.



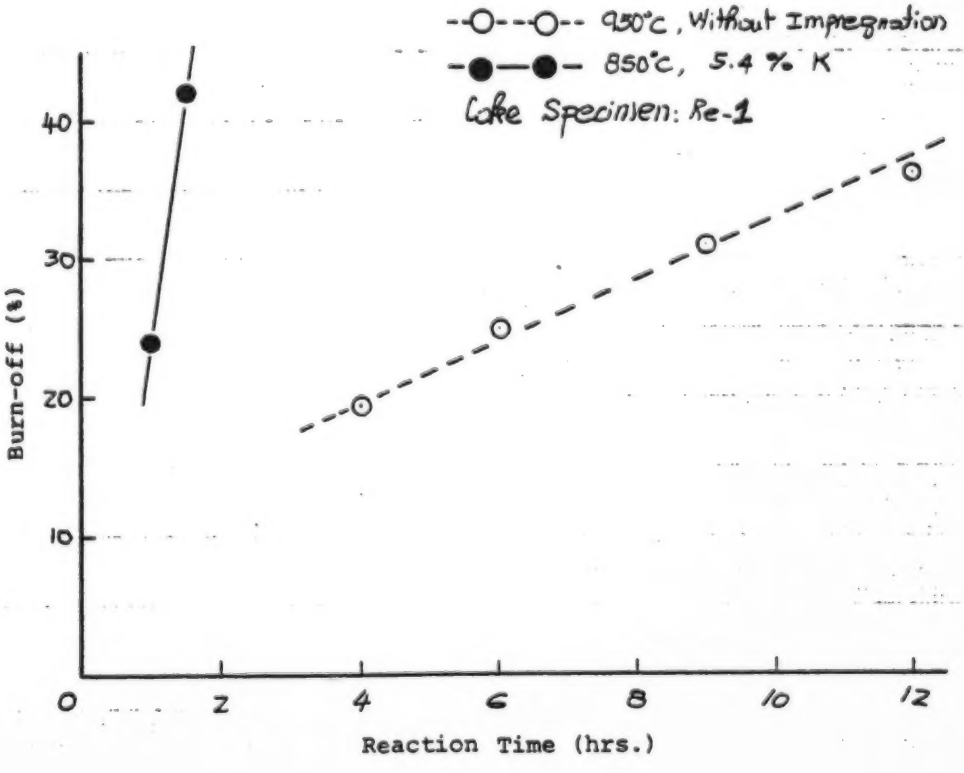


Fig. 22 Kinetics of oxidation of cokes Al-3 and Re-1 in $Ar/CO_2/CO$ mixture.

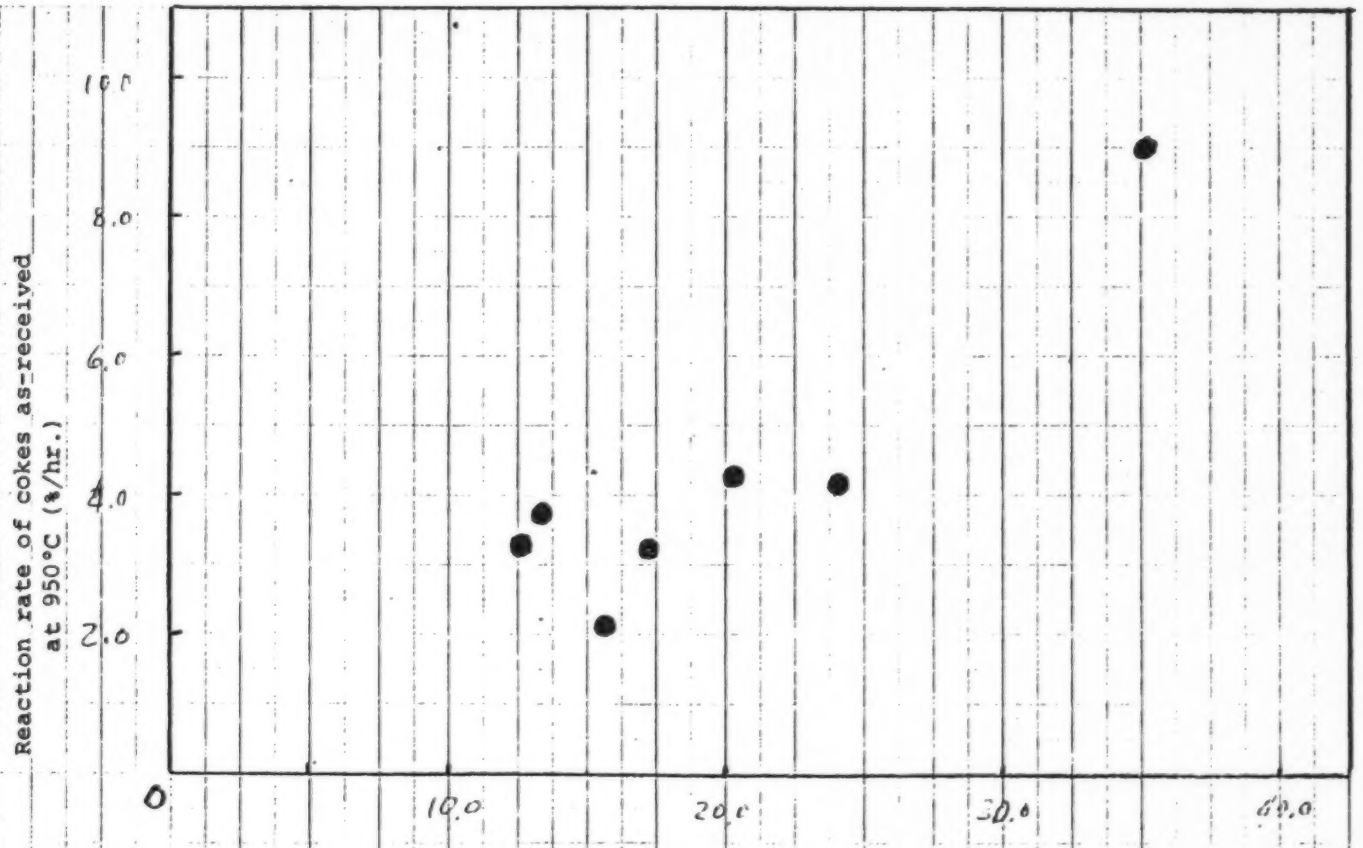


Fig. 23 Relationships between rates of oxidation with and without prior potassium impregnation.

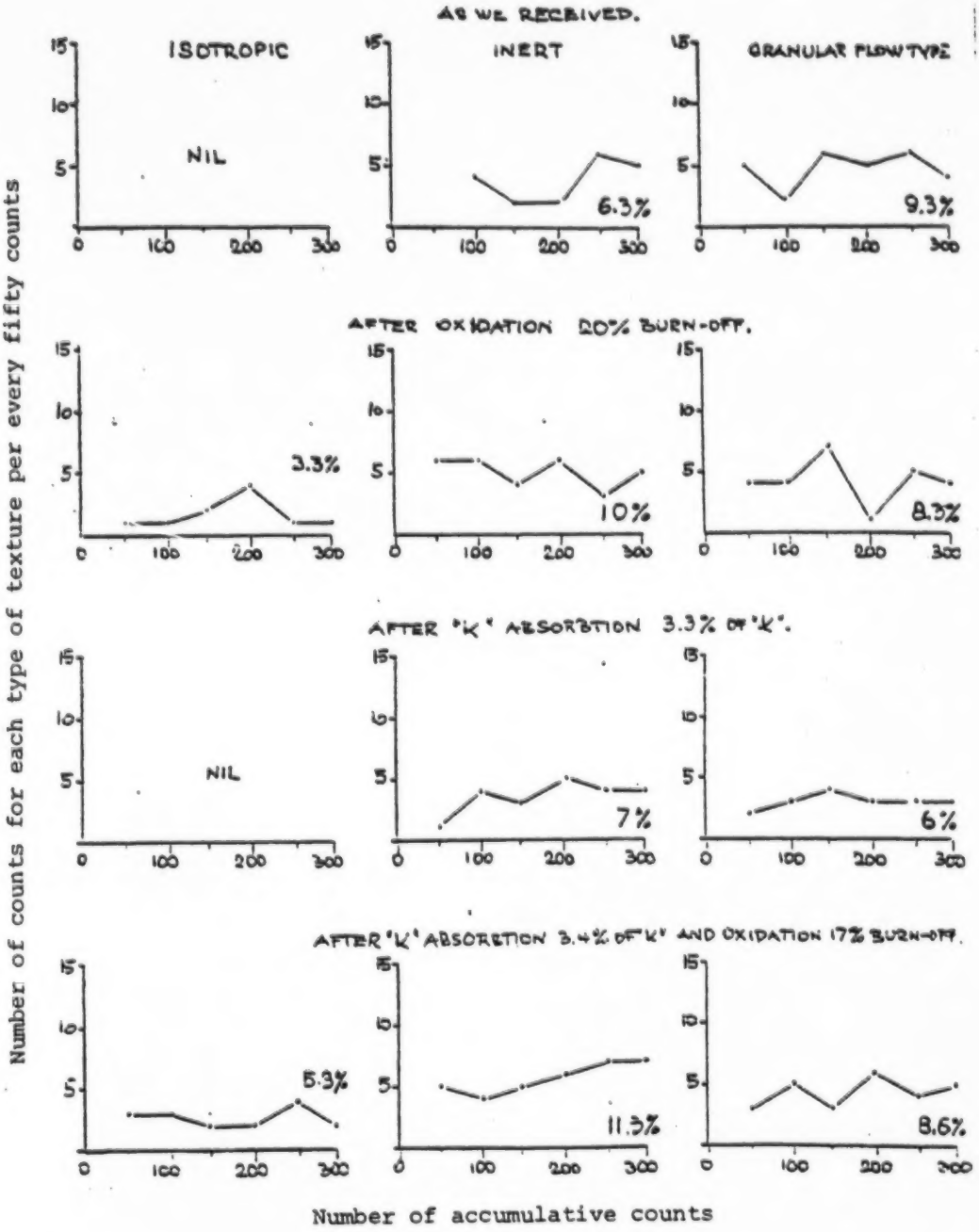


Fig. 24 Plots to show the convergence of optical texture analysis of Coke A1-1, before and after reactions.

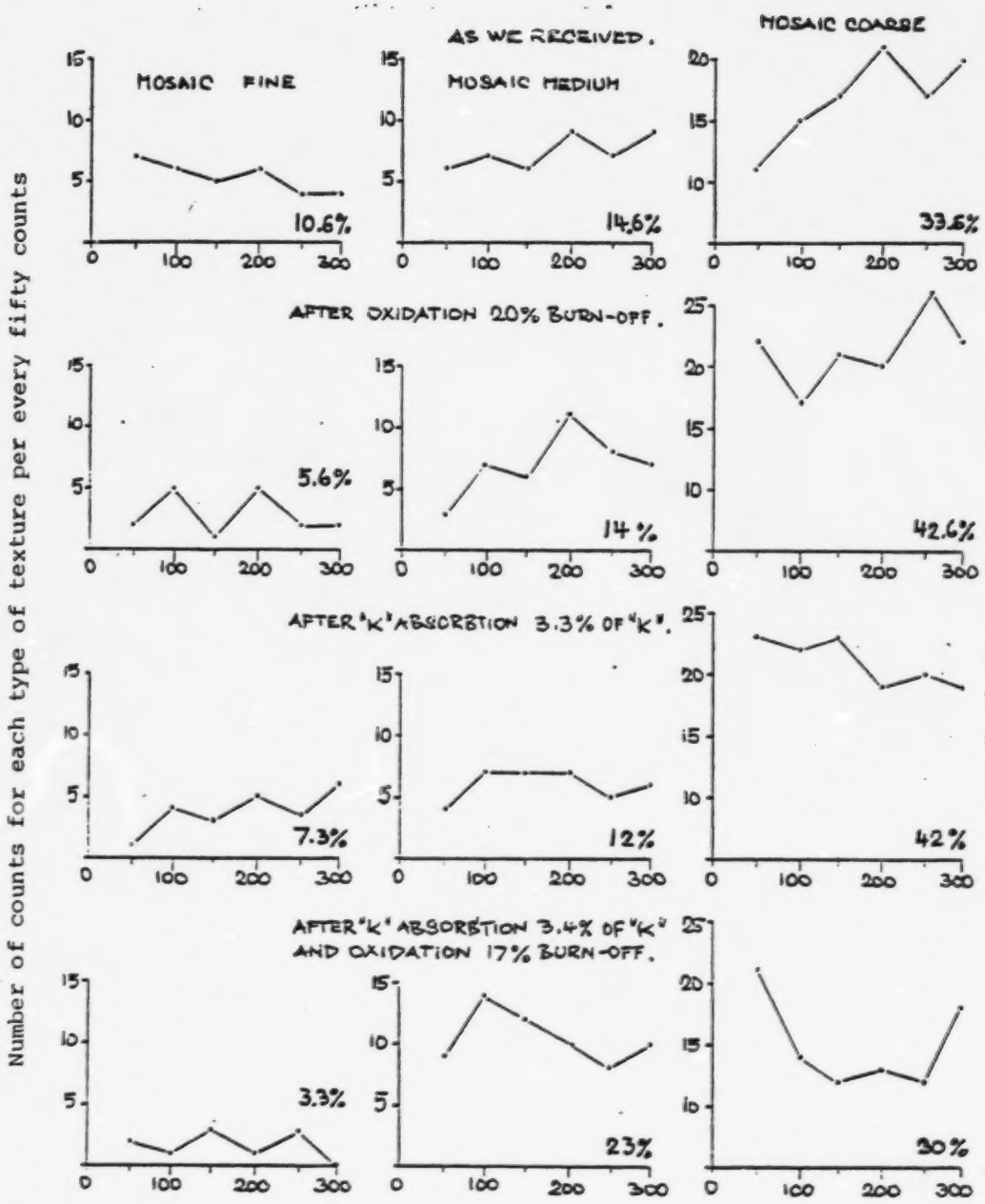


Fig. 24 - continued

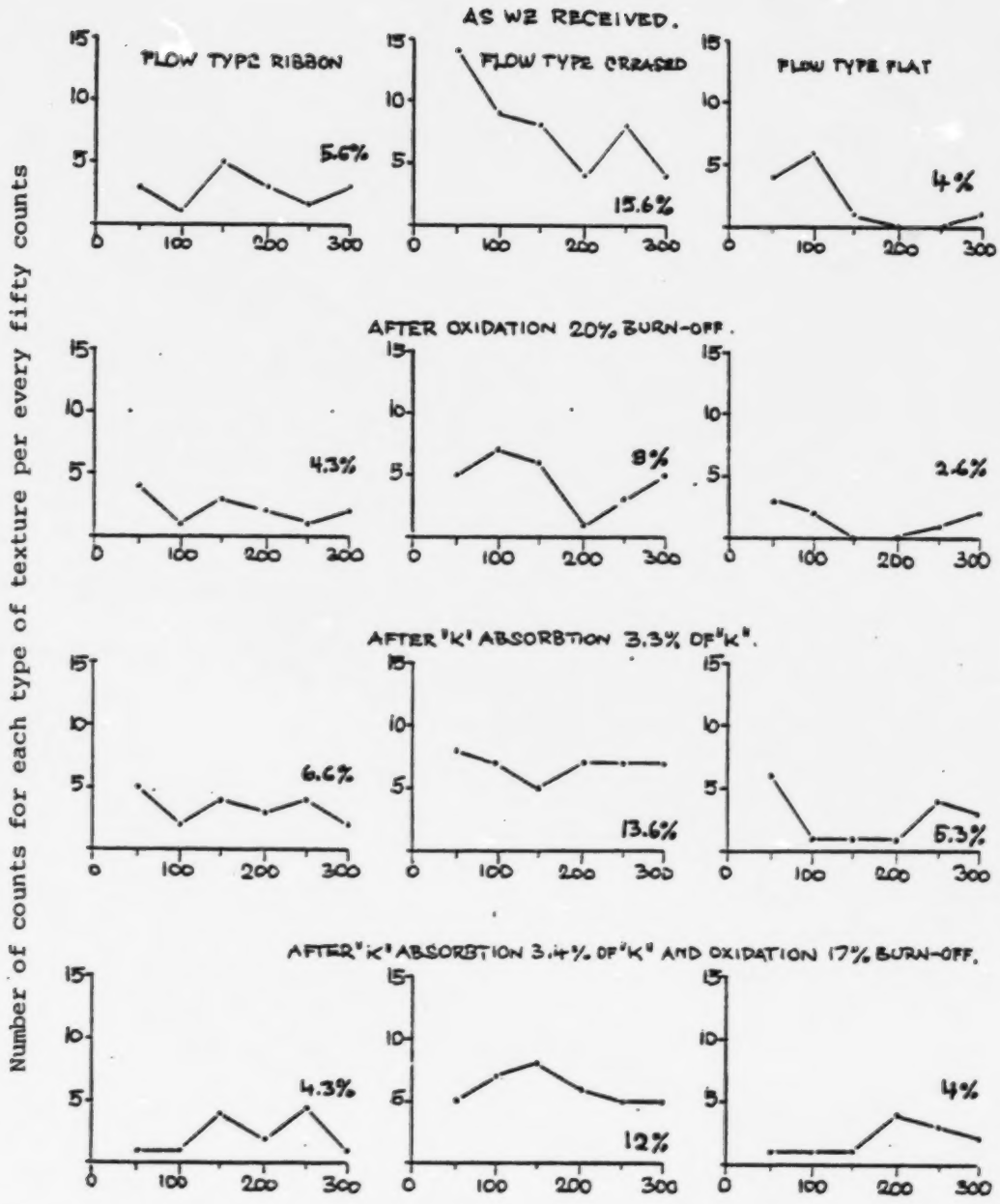


Fig. 24 - continued

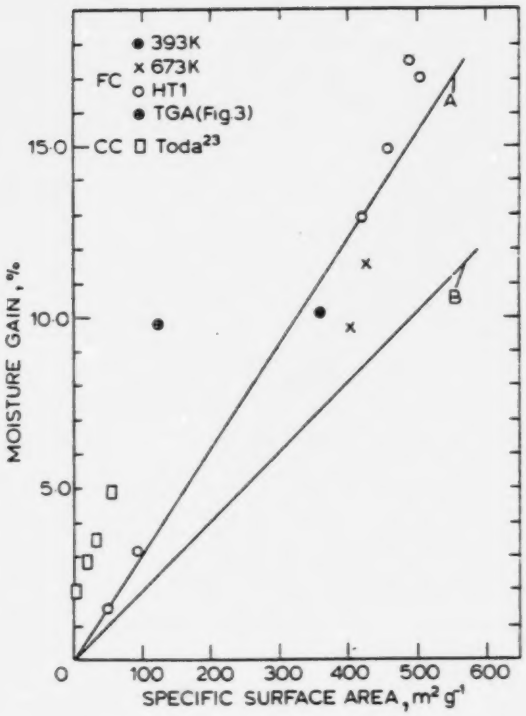


Fig. 25 Relationship between specific surface area and moisture gain for formed coke (FC) and conventional coke (CC); calculated lines A and B are based on cross-sectional areas 10.6×10^{-20} and 14.8×10^{-20} m^2, respectively (from Maru and Lu).

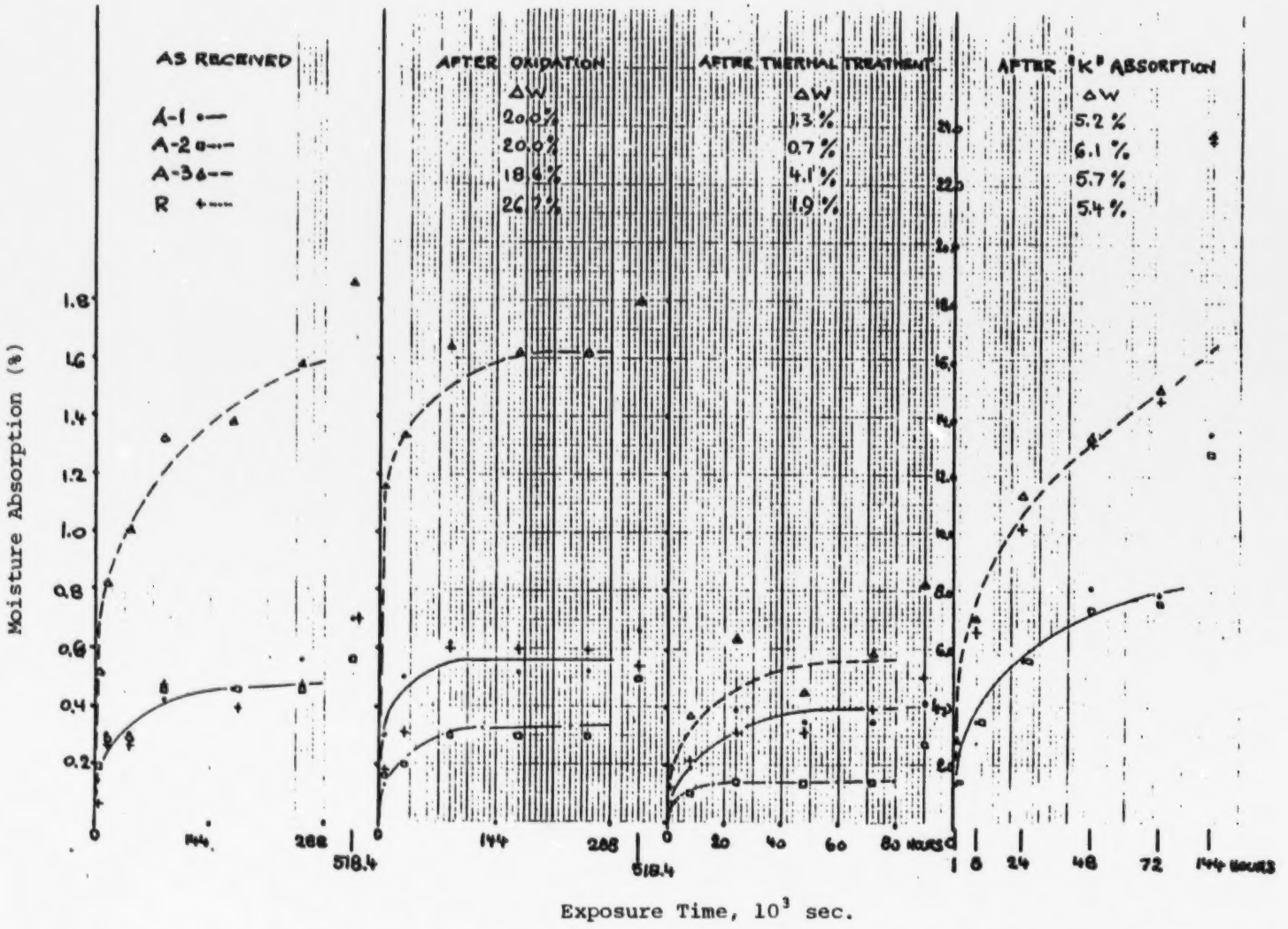


Fig. 26 The kinetics of moisture absorption by various coke specimens.

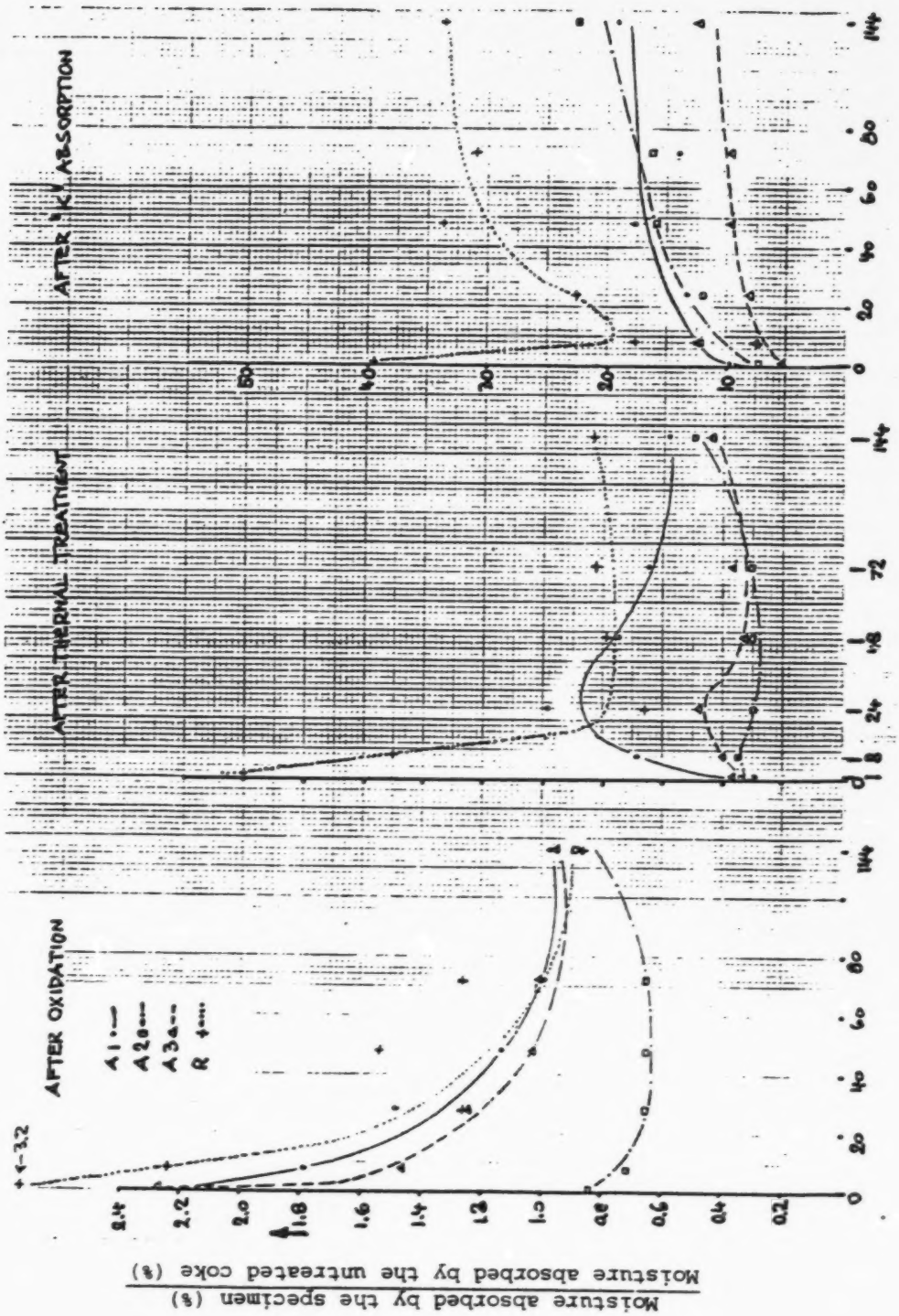


Fig. 27 Relative rate of moisture absorption with respect to coke as received.

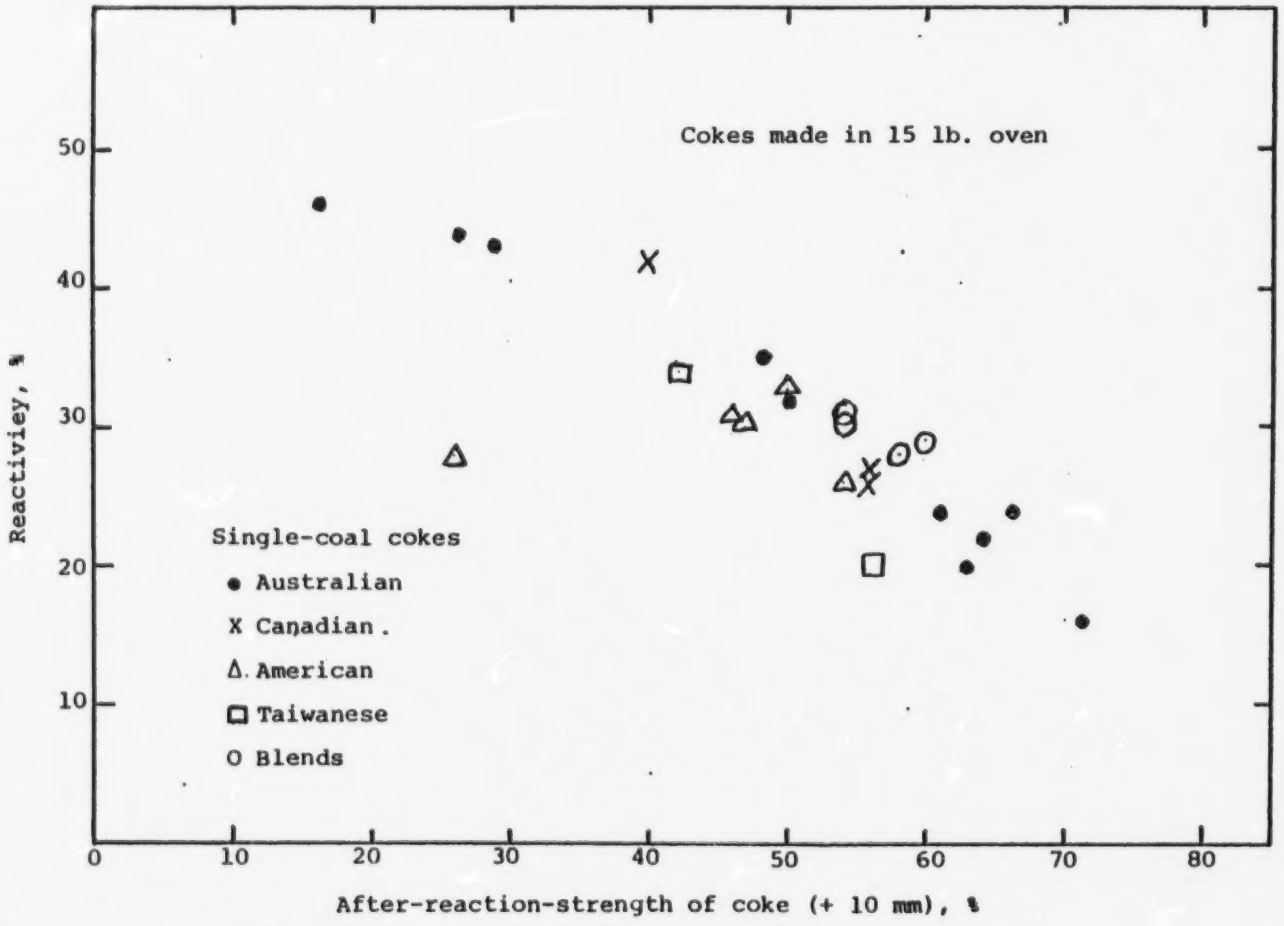


Fig. 28 Relationship between reactivity and coke strength after reaction. (From 6)

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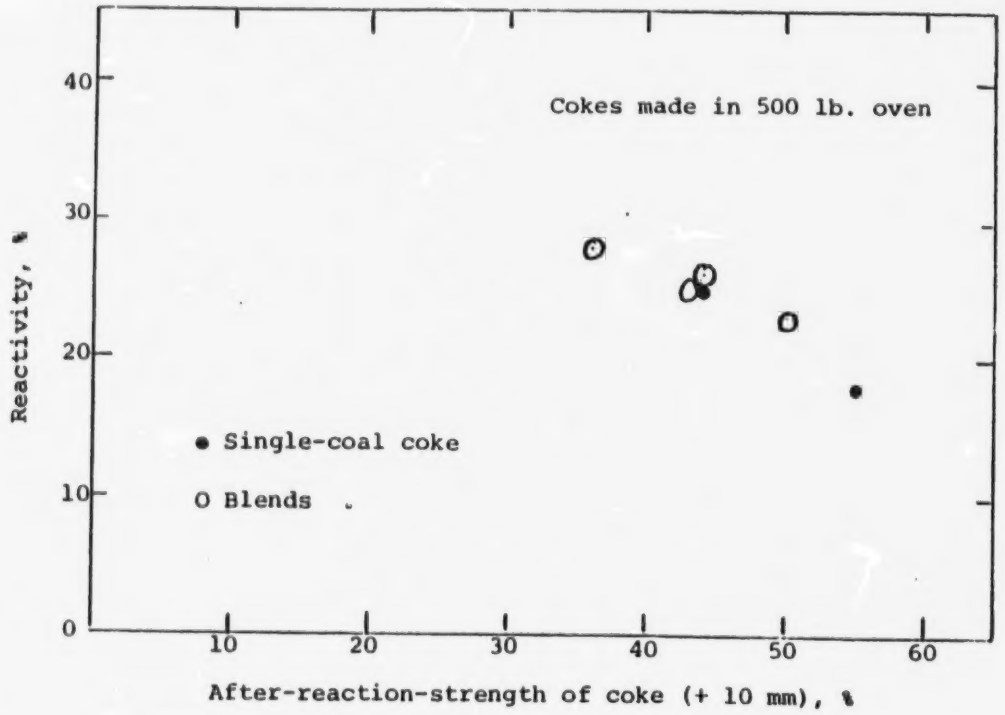

Fig. 29 Relationship between reactivity and coke strength after reaction.(from 6)